CRANFIELD UNIVERSITY

Max Bullock

Metaldehyde and its relationship with groundwater contamination and landfill leachate

School of Applied Sciences
MSc by Research

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Academic Year: 2013 - 2014

Supervisors: Peter Jarvis and Frédéric Coulon
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ABSTRACT

Increasing attention is directed towards many chemicals and microbial constituents which have not been historically considered as contaminants. These “emerging contaminants” are commonly derived from municipal, agricultural and industrial wastewater sources and pathways. Among others, metaldehyde, a widely used molluscicide, has been detected in groundwater at levels exceeding the 0.1 µg L^{-1} limit required by the Water Framework Directive. This has raised concerns for drinking water treatment, as the compound cannot be removed with conventional granular activated carbon or ozonation treatment processes.

Further to this, some recent case studies on groundwater quality reported metaldehyde concentrations > 0.1 µg L^{-1} in the vicinity of landfill sites. In all cases, there is no evidence or record of metaldehyde disposal. This growing evidence raises the question about the relationship between the characteristics of leachate generated from the landfill sites, the presence of metaldehyde and its impact on surrounding groundwater resources.

In the present study, two landfill sites located in the UK are being investigated as potential sources of contamination to groundwater by metaldehyde. In both cases, metaldehyde concentrations exceeded the levels expected from a point-source contamination site. For this reason, landfill leachate chemistry was assessed to determine whether an *in situ* synthesis of metaldehyde can occur within landfill sites.

A critical review found that potential reagents such as acetaldehyde, catalysts such as acetic acid and environmental conditions are present in groundwater aquifers. However, lab-based experiments have suggested that metaldehyde cannot be synthesised in the environment despite the presence of a wide range of pH values, cold temperatures, a high concentration of acetaldehyde, and the presence of a calcium bromide catalyst. This finding, combined with data

collected from the two case study sites over a 7 month period suggest that a point source of the pollutant is the most likely explanation.

The *in situ* testing also highlighted that the acetaldehyde reagent contained significant contamination by metaldehyde, of which the supplier was unaware. Two independent laboratories also confirmed the presence of metaldehyde in the reagent. Acetaldehyde of a purer grade from other manufacturers was also tested and found to contain significant levels of metaldehyde. These findings demonstrate another potential source of metaldehyde which is not agricultural. Finally, leachate from another UK landfill site was also analysed for metaldehyde to determine how prevalent metaldehyde contamination could be across landfill and was found to be present well above the limit for drinking water.

Keywords: Emerging contaminants, *In situ* synthesis, acetaldehyde contamination, metaldehyde organic mechanism, micropollutants

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1 Introduction

Increasing attention has been paid to various pollutants in groundwater in recent years due to a rising concern for public health with regards to drinking water and an improvement in the efficacy and sensitivity of the analytical techniques available. Whilst the concern over the presence of pollutants in drinking water and groundwater has long been considered, an increasing number of previously undetected organic pollutants such as pesticides and pharmaceuticals have been observed in the aqueous environment (Stuart et al., 2011). Several of these trace contaminants, termed 'micropollutants', are restricted in the aquatic environment under the Water Framework Directive (2000/60/EC) and Groundwater Directive (80/68/EEC) introduced by the European Commission (EC, 2013). The Drinking Water Inspectorate in England and Wales enforces European legislation on contaminants in drinking water. For pesticides, this limit is 0.1 μg L^{-1}. This requires that water companies demonstrate that they are taking action to reduce the concentrations of various pesticides in drinking water (DWI, 2013). Understanding the pathways and sources of these micropollutants is essential in developing ways to limit and control the amount of pollutant released into the environment and making its way into drinking water.

Sources of micropollutants in groundwater range from landfill leachate (Boretone et al., 2013), agricultural and industrial release (Barth et al., 2007), transport systems such as roads and railway and other urban infrastructure. Contamination of groundwater primarily occurs from either a point-source, being a site from which contaminants originate, often defined by its historical or current use (i.e wastewater treatment plant or a landfill site) or a non-point source, such as storm drainage, agricultural runoff and atmospheric deposition (Stuart et al., 2011). Other, more indirect causes of groundwater pollution are habitat modification (de-vegetation and land-drainage) and hydrologic modification (abstraction, mining and irrigation) (Ritter et al., 2011).

Evidence of groundwater contamination by micropollutants has been observed in two groundwater pumping stations located in the United Kingdom (UK), which

are used for the supply of drinking water. Whilst many organic contaminants are removed by granular activated carbon (GAC) and ozonation techniques, one detected compound, metaldehyde, cannot be effectively removed using this technology and therefore has the potential to exceed the < 0.1 µg L^{-1} drinking water limit set by the European Commission (Water UK, 2013). Both of the affected pumping stations are also believed to be located within the contaminant plume of disused landfill sites (LFS). Historical information on the waste deposited at the LFS, though very limited, suggests that metaldehyde was not disposed of at either of these sites. This information, combined with other anecdotal evidence of unexpected metaldehyde detections in the vicinity of landfill sites in Switzerland and Sweden, has raised questions on the link between landfill sites and groundwater contamination by metaldehyde. It has been suggested that the compound may be synthesised naturally in the environment (with influence from LFS), rather than a direct point-source from waste metaldehyde.

2 Aims and objectives

The aim of this project is to investigate the relationship between metaldehyde and groundwater contamination and explore how this relationship is affected by the presence of landfill sites:

Objective 1: Complete a critical review of existing data and scientific literature to understand the history of metaldehyde detections, sources of contamination, the chemical composition of landfills and leachate and to assess the feasibility of an *in situ* reaction for metaldehyde synthesis.

Objective 2: Gather new evidence data from both landfill sites to compare the degree of contamination and assess the plausibility of an *in situ* reaction. The primary compound of interest will be metaldehyde, however, other data such as dissolved oxygen, conductivity and pH will also be collected where possible.

Objective 3: Investigate the feasibility of the *in situ* reaction for metaldehyde synthesis using lab-based trials. Simulations of the industrial conditions within a

groundwater matrix will be assessed alongside real leachate samples to determine the parameters required for metaldehyde synthesis in landfill.

Following a literature review of the chemical composition of landfill leachate, metaldehyde, and the theoretical likelihood of its *in situ* synthesis. Two case study sites with a metaldehyde issue will be presented and discussed, followed by the assessment of the feasibility of the *in situ* reaction using laboratory testing.

3 Literature Review

3.1 Introduction

The growing concern for public health with regards to drinking water and the development of new analytical techniques has caused an increasing number of previously undetected organic pollutants, such as pesticides and pharmaceuticals, to be observed in the aqueous environment (Stuart et al., 2011). These compounds are often referred to a 'micropollutants', and are restricted in the aquatic environment under the Water Framework Directive 2000/60/EC (WFD) and Groundwater Directive (80/68/EEC), which were introduced by the European Commission (EC, 2013). Micropollutants are defined as organic or mineral substances whose toxic, persistent and bioaccumulative properties may have a negative effect on the environment and/or organisms. Their presence in aquatic mediums such as groundwater has been highlighted at extremely low concentrations, hence the term micro-pollutant (Degremont, 2013). The Drinking Water Inspectorate of England and Wales (DWI), a government regulator who ensures that drinking water quality is safe for consumers, has also required that water companies demonstrate that actions are being taken to reduce the concentrations of various pesticides in drinking water (DWI, 2013). Understanding the pathways and sources of these micropollutants is essential in developing ways to limit and control the amount of pollutant released into the environment and making its way into drinking water.

Sources of micropollutants in groundwater range from landfill leachate (Boretone et al., 2013), agricultural and industrial release (Barth et al., 2007), transport systems such as roads and railway and other urban infrastructure. Contamination of groundwater primarily occurs from either a point-source, being a site from which contaminants originate, often defined by its historical or current use (i.e wastewater treatment plant or a landfill site) or a non-point source, such as storm drainage, agricultural runoff and atmospheric deposition (Stuart et al., 2011). Other, more indirect causes of groundwater pollution are habitat modification (de-vegetation and land-drainage) and hydrologic modification (abstraction, mining and irrigation) (Ritter et al., 2011).

The fate, persistence and transport of micropollutants is an on-going area of research, however sufficient evidence has allowed some contaminant pathways to be established. Contamination directly to the groundwater from a point-source, such as a cesspool, septic tank or landfill site is very common and well documented. For example, several remediation projects exist within the UK to treat landfill leachates and reduce the levels of contamination from landfill sites to the surrounding environment (Robinson and Olufsen, 2007). Similarly, in the United States of America (USA), cesspools and septic tanks are considered as the primary sources of wastewater released directly into groundwater (Ritter et al., 2011). This situation is particularly common among older installations that were built prior to the Landfill Directive (99/31/EC), before which effective barriers protecting the water reserves from contamination were not required. Contamination in such instances is caused by pollutants dissolving in percolating rain and moisture contained within the waste, which then migrates into aquifers via the natural groundwater flow (Shand et al, 2007)

Contamination of groundwater can also occur through the mixing of surface waters with groundwater aquifers, particularly during periods of low rainfall where groundwater reserves are the primary sources for maintaining the flow of rivers. During these periods, any contamination of the surface water makes groundwater particularly susceptible to contamination from non-point sources such as agricultural or urban run-off. Changes in groundwater chemistry can

also have consequential effects on the established geological equilibriums in aquifers, also referred to as ‘baseline concentrations’. An example of this would be the resulting higher carbonate concentrations in chalk aquifers where acidic leachate has entered the water (Shand et al, 2007). The aggressive acidic conditions affect the equilibrium of dissolved chalk, causing more solid chalk to dissolve. This can then potentially cause further changes in aquifer chemistry, as the eroding rock allows older, previously confined aquifers to mix with contaminated aquifers (Shand et al, 2007).

Several legislative drivers require actions to be taken to limit and monitor the release of contaminants into the environment. The Pollution Prevention and Control Act 1999 requires that pollution from industry, including landfill sites, is minimised. The Groundwater directive (80/68/EEC, 2006) requires that contaminants entering groundwater are monitored and minimised to acceptable threshold values. The Water Framework Directive, adopted in 2000, has also set out objectives to address concerns raised by the European populace to protect clean waters from current and future pollution. These directives and regulations also work alongside the Drinking Water Directive (98/83/EC), which requires that drinking water quality be based on the latest scientific evidence, its quality be monitored and enforced, consumers remain informed and that it contributes to the wider EU water and health policies, such as those discussed above. The DWI requires all water companies to provide them with full details of their annual performance and ensuring that they meet these requirements. This pressure has required the implementation of investigation strategies by water companies to assess the extent of contamination from emerging micropollutants. Particular attention is being paid to metaldehyde, which has seen unexpectedly high concentrations in the groundwater (Cooper and Warrington, 2013).

This literature review to follow, investigates the sources, fate and occurrence of emerging organic contaminants in groundwater with particular focus on metaldehyde and landfill leachates. Where possible, existing data on metaldehyde concentrations in ground and surface waters was analysed and

key parameters influencing the fate and transport of this compound identified. Studies on groundwater contaminated by landfill sites were reviewed further to assess the primary contaminants and the prevalence of emerging organic contaminants, along with the fate of these compounds and the way they are transported through the environment.

In order to investigate concerns raised regarding the relationship between landfill sites and metaldehyde concentrations in groundwater, key organic compounds identified in landfill leachate are investigated to determine whether they provide appropriate reagents to synthesise metaldehyde. Other environmental variables associated with landfill sites, such as temperature and presence of a catalyst are also investigated to compare with the conditions used in the industrial manufacture of metaldehyde, such as an abundance of acetaldehyde reagent, acidic and metallic catalysts and low temperatures. Furthermore, a plausible mechanism of *in situ* synthesis of metaldehyde is proposed, based on existing data.

3.2 Landfill sites and leachates

To assess the feasibility of an *in situ* synthesis of metaldehyde, an understanding of leachate chemistry must be obtained in order to determine the likelihood of appropriate reagents and conditions being present. Landfill leachate is the liquid that drains or 'leaches' from a landfill; it varies widely in composition regarding the age of the landfill and the type of waste that it contains (Kjeldsen et al., 2002). The primary component of landfill leachate is water but it is typically found to contain dissolved organic and inorganic chemicals along with suspended solids. Leachate can be generated from liquid contained within the waste, such as moisture, petrol and other organic solvents and excess rainwater percolating through the waste layers to the base of the landfill cell. The physical, chemical, and microbial processes occurring in the waste material can transfer pollutants into the percolating water and ultimately into groundwater sources (Kjeldsen et al., 2002). The *in situ* theory would therefore require that these various changes within the landfill would promote

the formation and consequent leaching of the synthesised metaldehyde into the groundwater. Leaching to groundwater is found to be more common in older landfill sites where no effective barrier was installed to protect the groundwater from contaminants, though different degrees of contamination have still been reported in barrier-protected landfills (Tuncer, 2003).

The chemical analysis of landfill leachate usually consists of the following:

- Chemical oxygen demand (COD, the total amount of compounds in the water which can be oxidised, organic and inorganic)
- Total organic carbon (TOC, the total amount of organic carbon in the water),
- Biological oxygen demand (BOD, the amount of organic compounds which can be readily broken down by aerobic bacteria)
- pH
- Suspended solids and
- Heavy metals such as lead, nickel and arsenic.

To highlight the complexity and the impact that several variables can have on leachate chemistry, an example of a raw leachate analysis from two landfill sites located in the UK (LFS A, located in the south of England, and LFS B, located in the northwest of England) is shown in Table 1. It is evident that variation of season (highlighted by the higher leachate strength being observed in LFS A in the summer, perhaps due to less dilution from rainfall resulting in a more highly concentrated leachate) and landfill age (highlighted in LFS B by the large difference in leachate strength after a 5 year gap) both have a direct influence on the leachate quality. However it should be noted that leachate strength can also be impacted by several other factors such as mechanical (efficacy of the leachate collection), geological (the properties of the natural materials surrounding the landfill) and meteorlogical (the climatical events experienced by the site). Leachate strength will be important in any *in situ* synthesis of metaldehyde as it is effectively the 'potency' of the chemical mixture providing the reagents for the reaction. A stronger leachate is likely to contain a greater

variety of compounds at a higher concentration and therefore provide reagents and conditions required for an *in situ* synthesis.

Mecoprop, a herbicide and an emerging organic contaminant was also detected in the summer of 2007 in LFS B in the μg L^{-1} (ppb) range . This further highlights the complexity of leachate chemistry and the difficulty in eliciting a full chemical profile of a leachate, as micropollutants are rarely looked for during routine analysis of leachate and usually require a targeted analytical method, as is the case with metaldehyde.

Table 1: An example of leachate composition from two landfill sites in the UK (Enviros Consulting)

Parameter	**LFS A (Winter 2005)**	**LFS A (Summer 2005)**	**LFS B (Spring 2003)**	**LFS B (Summer 2007)**
COD (mg L^{-1})	1610	1760	5990	22440
TOC (mg L^{-1})	560	533	1240	6200
BOD (mg L^{-1})	103	115	688	9632
pH	7.4	8.1	8.3	8.0
Suspended solids (mg L^{-1})	106	218	-	-
Lead (μg L^{-1})	6	17	0.1	0.1
Nickel (μg L^{-1})	138	136	0.7	0.4
Arsenic (μg L^{-1})	21	6	<0.01	-
Phenol (mg L^{-1})	-	-	-	22.9
Mecoprop (μg L^{-1})	-	-	-	183

To further demonstrate how leachate properties such as COD, BOD and dissolved metal concentrations can vary in between different leachates, a wider view of the range of leachate properties can be found in Table 2. This study by Kjeldsen et al. (2002) collected leachate data from several landfill sites in various countries and calculated a range of values for each parameter. These parameters are the main indicators of leachate strength and landfill age. They

therefore provide values which can be expected from landfills located in different climates around the world and of varying ages. It is therefore likely that if *in situ* synthesis does occur, it will happen in leachate with properties inside this range.

Table 2: Leachate composition (Kjeldsen et al, 2002)

Parameter	Range
COD (mg L^{-1})	140 – 152000
TOC (mg L^{-1})	30 – 290000
BOD (mg L^{-1})	20 – 57000
pH	4.5 – 9
Total solids (mg L^{-1})	2000 – 60000
Lead (mg L^{-1})	0.001 – 5
Nickel (mg L^{-1})	0.015 - 13

As well as these broad indicative types of analysis, substances known as Xenobiotic organic compounds (XOCs) are sometimes reported. XOCs are defined as substances which are foreign to a biological system (Thakur, 2006). Contaminants categorised in this way include herbicides and pesticides such as mecroprop and metaldehyde and industrial solvents such as benzene and chlorinated alkanes. Most, if not all, emerging organic contaminants and micropollutants fall under this category. XOCs are usually targeted in leachate as they are generally hazardous substances that can cause harm to aquatic organisms and the natural environment, and can cause health concerns if they enter drinking water. Due to the complex matrix of organic contaminants found in leachates, several types of analysis such as Gas Chromatography, with both Mass Spectrometry (GC-MS) and Flame Ionisation (GC-FID) detection, and High Performance Liquid Chromatography (HPLC) must be used to thoroughly detect, characterise and quantify contaminants in leachate. This instrumentation is often not able to differentiate between various compounds in a single analysis, so full leachate characterisation can be problematic (Beldean-Galea et

al, 2013). Table 3 gives an example of XOCs identified in leachates. From this particular study, it is evident that the majority of the detected substances are non-polar, with low degrees of water solubility. Polar compounds such as metaldehyde and benzamide tend to give lower recovery rates in analytical methods, making analysis problematic (Beldean-Galea et al, 2013). Polar compounds are therefore difficult to detect in leachate screening tests without specific extraction methods. This is further highlighted by the lack of published data on metaldehyde in landfill leachate.

Table 3: Examples of Xenobiotic Organic Compounds (XOCs) found in landfill leachate

Xenobiotic Organic Compound	Classification or use	Concentration range (µg L^{-1})
Benzene	Industrial solvent	0.2 – 1630
Toluene	Industrial solvent	1 – 12300
Naphthalene	Fumigant (moth-balls), industrial synthesis	0.1 – 260
Xylenes	Industrial solvent	0.8 – 3500
Chlorobenzene	Industrial reagent/solvent	0.1 – 110
Dichloromethane	Paint stripper and industrial solvent	1.0 – 827
Trichloromethane (chloroform)	Industrial solvent, anaesthetic (historical)	1.0 – 70
Phenol	Chemical precursor (plastics, pharmaceuticals)	0.6 – 1200
Cresols	Chemical precursor (plastics, pesticides)	1 - 2100
AMPA	Pesticide	3.8-4.3
Bentazon	Pesticide	0.3 – 4.0
Mecroprop	Pesticide	0.38 – 150
Diethyl phthalate	Plasticiser	0.1-660

The large concentration ranges observed for compounds such as benzene can be explained, as XOCs are synthetic compounds or decomposition products of synthetic compounds. Therefore, their presence in leachate depends primarily

on how much of it was disposed of. Differences in waste disposal legislation between different countries is also likely to have an impact on the presence of XOCs in landfill, as tighter controls on hazardous waste would result in safer disposal with less environmentally damaging outcomes. However most landfill sites which cause issues were constructed before such restrictions were in place, such as Pollution Prevention and Control Act 1999.

As leachate is formed by percolating rainwater and the biological breakdown of waste material, contaminant concentrations are closely linked to meteorological conditions, in particular rainfall and temperature. A study of two landfill sites in Lithuania gave particular attention to the relationship between rainfall and leachate properties (Baziene et al, 2013). It was observed that concentrations of chloride (Cl-), sulphate (SO_4), ammonia (NH_4), zinc (Zn) and nickel (Ni) in the groundwater were considerably higher when rainfall was lower, suggesting that the release of these chemicals is relatively constant, and that rainfall simply dissolves the contaminants as it percolates. This was also observed during the initial investigation at one of the landfill sites in this project. Additionally, leachate concentrations were found to be higher in samples taken closest to the point-source (the landfill cell). Lower contaminant concentrations were observed further from the point source due to mixing with uncontaminated groundwater along the contaminant pathway. The results from this study also generally agreed with Kjeldsen et al (2002) and observations made by Palmisano and Barlaz (1996) that heavy metal content of a leachate sample is dependent on the pH of the sample. This is due to the increased solubility of metals at lower pH and organic compounds acting as chelating agents, dissolving metals which would otherwise be insoluble. Periods of lower precipitation also correspond with lower pH, which is likely to be caused by higher acid concentration in the percolating water.

A study carried out in China (Fang et al, 2012) aimed to characterise the odours released from different areas of a landfill. Though this data will not be directly comparable with leachate and groundwater studies, it can help to understand the composition of some of the more volatile and polar substances in landfill,

which may be overlooked in other studies. The landfill site in this study featured areas of active tipping and older closed areas, as well as leachate storage and gas extraction, which led to the data showing a large range of potential contaminants at various stages of disposal. Results from this study indicate the presence of compounds that could potentially act as precursors for a possible *in situ* synthesis of metaldehyde (primarily partially oxidised polar compounds, such as carboxylic acids and aldehydes; see Table 4).

The two active tipping sites (A and B) were located 100 m from each other in an area where approximately 7600 tons of unsorted waste was piled up and compacted each day. The closed area with gas extraction was covered with a polymer membrane to prevent percolating rainfall and the escape of gases. The age of the waste in this area was recorded as being more than three years. The leachate area samples were taken from the storage and disposal pools.

Table 4: Examples of leachate components which could provide evidence of an in situ synthesis of metaldehyde (Fang et al, 2012)

Chemical	Area of detection	Concentration ($\mu g\ m^{-3}$)	Comments
Ammonia	Active tipping A Active tipping B Gas extraction of closed area Leachate storage pool Leachate disposal pool	900 1800 1800 1800 1800	Ammonia is formed by the breakdown of fats and proteins. This compound is of particular interest as its high pH is likely to hinder any *in situ* formation of metaldehyde
Toluene	Active tipping A Active tipping B Gas extraction of closed area Leachate storage pool Leachate disposal pool	6.1 46.1 8.1 4.2 6.4	Though toluene could be a breakdown product, it is more likely to be inherently present in the waste due to its use in industry. Therefore, higher values are observed in active tipping where the least chemical breakdown and diffusion has occurred.
m-Xylene	Active tipping A Active tipping B	112 112	Like Toluene, this compound would be inherently present in the waste, so it was only detected in active tipping.
Acet-aldehyde	Active tipping A Active tipping B Gas extraction of closed area Leachate storage Leachate disposal	7.7 28.4 69.9 13.6 8.7	Most likely formed by carbohydrate decomposition, it is also present in many forms of plant life and can be a by-product of fermentation. This compound is of particular interest to this study as it is the most likely precursor for *in situ* metaldehyde synthesis. It's presence in older landfills and leachate is also significant. Note that concentrations are higher in decomposing waste.
Butyl-aldehyde	Active tipping A Active tipping B Gas extraction of closed area Leachate storage Leachate disposal	87.7 57.3 88.6 27.1 8.5	Most likely formed by carbohydrate decomposition. This compound was highlighted in order to show how aldehyde compounds can form in landfill. The concentrations are higher in

			decomposing waste from the gas extraction.
Acetic acid	Active tipping A Active tipping B Gas extraction of closed area Leachate storage Leachate disposal	1260 2090 712 767 1130	Formed from decomposing sugars under more aerobic conditions by acetogenic bacteria. Concentrations are higher under the earlier aerobic conditions in landfill. Carboxylic/fatty acid compounds will be relevant to this study as they would be the primary catalysts driving a potential *in situ* formation of metaldehyde. The presence of acetic acid could also be caused by the oxidation of acetaldehyde.
Butanoic acid	Active tipping A Active tipping B Gas extraction of closed area Leachate storage Leachate disposal	14.8 64.9 17.3 22.0 9.5	As with acetic acid, these acids are commonly formed in landfill, and would be a likely primary catalyst for an *in situ* synthesis.

This study provides insight into some of the more volatile, polar and water-soluble compounds which can be overlooked in other studies into leachate characterisation. It also provides some of the stronger evidence for a potential *in situ* metaldehyde synthesis from acetaldehyde, acids and metallic and ionic catalysts, which is discussed later in the review.

3.3 Chemical changes in landfill sites and leachate over time

For the feasibility of *in situ* synthesis of metaldehyde to be assessed, the changes in the chemical and biological processes within the landfill must be addressed. The review by Kjeldsen et al (2002) provides information on the various stages of landfill decomposition.

The compaction of municipal waste at disposal and its biodegradability inevitably cause most landfills to become an anaerobic environment, as oxygen

from the air and waste is gradually consumed by aerobic bacteria. This gives rise to many similarities to the leachate composition across many different landfills. Therefore, landfill leachate components can generally be categorised into four different groups – dissolved organic matter, inorganic macro components, heavy metals and the previously discussed xenobiotic organic compounds (XOCs) (Kjeldsen et al, 2002). It is generally accepted that landfill sites undergo four stages of decomposition, these stages are as follows:

(1) An initial aerobic decomposition phase – this is where the initial degradation of the material occurs via hydrolysis and degradation by aerobic micro organisms. The residual oxygen in the waste is consumed by aerobic bacteria as the readily degradable organic material is consumed. Polymers of high molecular weight such as cellulose and fats, which do not readily permeate the microbial membranes (Palmisano et al, 1996), are eventually degraded to molecules of lower molecular weight. These resulting monomers (eg. soluble sugars and amino acids) are further fermented via microbial processes into carboxylic acids (potential sources of *in situ* catalysis). Oxygen levels deplete rapidly at this stage, resulting in anaerobic conditions. Leachate at this stage would comprise mostly of moisture released from compaction and liquid waste.

(2) Acidogenic stage– this phase begins when the immediately available oxygen has been consumed and no additional oxygen enters the covered and compacted system. Fermentative and acetogenic biological reactions begin to dominate and the pH of the leachate lowers from around 7.5 to 5.7 as soluble sugars provide the carbon source for microbial activity (Barlaz et al, 1996), producing carboxylic acids. This phase will also show the highest concentration of metals as they are dissolved due to the decreasing pH. The highest COD and BOD values are also observed at this stage. Leachate at this stage appears black and cloudy with a strong smell caused by fatty acids (Leachate, 2013).

(3) Accelerated methane production stage – As carboxylic acids are broken down in the anaerobic system, significant levels of methane are produced. The pH of the leachate and waste begins to rise at this stage as the acids are consumed and the presence of accumulated ammonia dominates.

(4) Decelerated methane production stage - The concentration of soluble fermentation products declines due to their conversion to methane, and methane production slows due to its dependence on the soluble media. The pH will continue to rise as acids are consumed and ammonia accumulates.

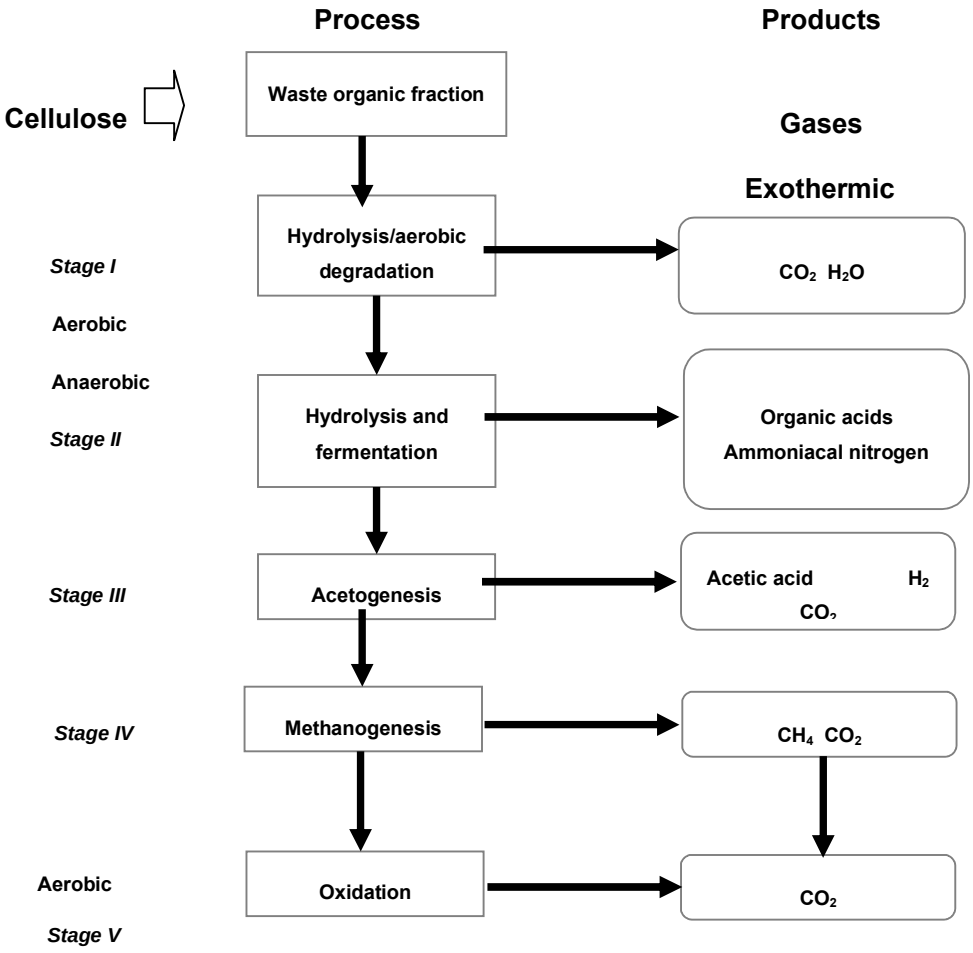


Figure 1: The major stages of waste degradation

The effect of these various phases on *in situ* synthesis of metaldehyde can be quite significant. A heavily aerated landfill cell is likely to cause significant breakdown of any metaldehyde formed, preventing it from being present in

detectable amounts. The likelihood of potential reagents such as acetaldehyde being present are also less, as fermentation reactions are not yet dominant. A landfill in the stable methanogenic phase is also less likely to produce metaldehyde as any potential acidic catalysts would have been consumed by the methanogenic bacteria. Metaldehyde synthesis is most likely to occur during the acidogenic phase (stage 2), where fermentative reactions have produced aldehydes and acids, and the residual oxygen around the reaction cell would be minimised, allowing metaldehyde to persist in the medium. It has been determined that it can take 20-50 years for a landfill to reach its stable methanogenic phase and that landfills in dryer regions can remain within the acid phase for decades or even longer (Kjeldsen et al, 2002).

3.4 Metaldehyde

Metaldehyde is a tetramer of acetaldehyde, which is used as a pesticide to target molluscs in arable farming (Eckert et al., 2012). Metaldehyde kills the molluscs by disrupting the production of their mucus membranes. The efficacy and economical benefits of the pesticide mean it is a popular choice among farmers (Simms et al., 2006; Edwards et al., 2009). The relatively fast degradation of the compound also makes its use more attractive than more persistent alternatives. The compound was also used as solid fuel for camping when industrial production began in the 1920s, however it's use is now primarily as a pesticide (Lonza, 2010). Metaldehyde is reported as having a half life of approximately two months (Edwards, 2006) which is believed to be due to microbial breakdown as sterilised soil was found to breakdown metaldehyde more slowly (Simms et al., 2006). Metaldehyde is therefore not regarded as a significant threat to groundwater contamination (PPDB, 2012), however increased persistence of this compound has been observed in the more anaerobic conditions of groundwater reserves where less degradation pathways are possible, allowing the compound to accumulate in the environment (Lapworth, 2012). Metaldehyde is typically applied to fields during the warm, wet season around September to October, and migration to surface and

groundwater is usually observed at this time from run-off and soil migration (Water UK, 2013). Metaldehyde was first introduced in 1940 and registered as a pesticide in 1967 (EPA, 2006). Though it has been controlled and regulated in the UK since 1980 due to its harm to domestic animals (HSE, 2014), it was not generally monitored as a potential contaminant in groundwater sources. In order to assess the extent of metaldehyde contamination in groundwater, most likely as a result of the restrictions set by the Water Framework Directive, a sufficiently sensitive analytical method was developed in 2007 (Water UK, 2013). Particular attention has been directed towards metaldehyde as it has been commonly detected in drinking and groundwater at levels exceeding the 0.1 µg L-1 requirement for pesticides in drinking water standard (Stuart et al, 2011). One of the problems with metaldehyde is the inability of most drinking water treatment processes to remove it effectively. For example, metaldehyde cannot be satisfactorily removed by conventional activated carbon or ozonation processes which are typically used for pesticide removal (Water UK, 2013; Tao and Fletcher, 2013).

Actions required by the DWI to demonstrate attempts to reduce metaldehyde concentrations to below 0.1 µg L-1 in drinking water have made it necessary for water companies to monitor and target the compound more intensively. With increasing anecdotal evidence from the UK, Switzerland, and Sweden it has been shown that metaldehyde concentrations in raw water do not always correlate with the expected seasonal fluctuations.

3.5 In situ metaldehyde synthesis theory

From work previously carried out at two sites in the UK (Hydrock and Affinity Water) and some anecdotal evidence from Sweden, Switzerland and other UK water companies, metaldehyde has been detected in significant quantities in aquifers passing through disused landfill sites, and in some cases surface waters. A recent study carried out by the British Geological Survey has shown the presence of both metaldehyde and paraldehyde from a flood plain aquifer of the river Thames, close to a disused landfill site (Stuart et al, 2011 b). Due to the frequent unexpected detections of metaldehyde in groundwater, part of this

project will determine whether metaldehyde can be synthesised from within the landfill site or aquifer, and not as a direct contamination from discarded pesticide or solid fuel.

The industrial production of metaldehyde is typically from the polymerisation of acetaldehyde with acidic conditions at low temperatures (Eckert et al., 2012), though similar processes using paraldehyde as a raw material are also used. It is well documented (Lonza patent US3403168) that the yield for metaldehyde in this reaction is low (around 8%), and that the smaller, less-polymerised compound paraldehyde is the most kinetically favourable product (around 80%). Under the industrial conditions, solid metaldehyde crystallises out of the liquid acetaldehyde (or paraldehyde) phase, and is regularly removed from the reaction vessel to force the chemical equilibrium to continuously crystallise and produce metaldehyde (Lonza, personal communication). Halides of alkaline earth metals, such as calcium bromide are catalysts for this reaction (Eckert et al., 2012). The primary reagent for this reaction, acetaldehyde, a volatile, naturally-occurring and water soluble aldehyde, has been detected in the gaseous emissions from closed, ageing landfill sites (Fang et al, 2012).

For the *in situ* reaction to successfully occur, there will ideally need to be a source of acetaldehyde and/or paraldehyde, acidic catalysts and low temperatures. The reaction-promoting conditions would also have to be maintained for the reaction mixture to reach an equilibrium which would be sufficient to produce metaldehyde at detectable levels (around 0.05 – 0.1 μg L^{-1}).

Conditions in groundwater aquifers typically range from 2 - 20°C (BGS, 2009), theoretically providing adequate temperatures for the acetaldehyde to polymerise. The contaminated aquifers studied in this project are predominantly chalk and limestone. It is therefore unlikely that conditions will be acidic enough to produce significant or detectable levels of metaldehyde due to the buffering effect of the carbonate rock (Shand et al, 2007). However, sufficient leaching from nearby landfill sites may be able to provide enough acidity to the reaction mixture, before the pH is raised again by the dissolving chalk. The higher

pressures experienced in the lower depths of aquifers may also push the reaction equilibrium towards the less entropic metaldehyde side of the reaction. However this theory may not be relevant if the metaldehyde is synthesised within the landfill site, and enters the aquifer via leaching.

As paraldehyde is the favoured product of the reaction, it is reasonable to assume that paraldehyde levels in the aquifer would exceed that of the metaldehyde if this reaction occurs *in situ*. Paraldehyde also has significantly higher solubility than metaldehyde, 1.12 x 10^5 mg/l compared to 188 mg/l (PPDB, 2012), so it would be predicted to have a higher rate of leaching from the landfill. However, the BGS study which detected both metaldehyde and paraldehyde in a flood plain aquifer showed that paraldehyde levels were consistently lower and that paraldehyde was not always detected alongside metaldehyde (Table 5; Stuart et al, 2012 b). This finding is also supported by the initial investigations carried into the metaldehyde problem at a site in Helpston, UK, by environmental consultants (Table 6). This therefore provides evidence against the theory of *in situ* metaldehyde synthesis, as even though paraldehyde was detected, it was well below the expected 80% yield. It has also been suggested that the trace detections of paraldehyde may also arise from the degradation of metaldehyde inside the analytical instrument due to the high injection temperatures (Affinity Water, personal communication).

Table 5: Metaldehyde and Paraldehyde detection in a flood plain aquifer (Stuart et al, 2012)

Compound	**Detection frequency (total of 12 samples taken)**	**Maximum concentration (µg $L^{-1)}$**
Metaldehyde	7	>1
Paraldehyde	5	>0.1 but <1

Table 6: Paraldehyde and Metaldehyde concentrations from a contamination aquifer (Cooper and Warrington, 2013)

Sample	Metaldehyde concentration (µg L^{-1})	Paraldehyde concentration (µg L^{-1})	Paraldehyde/Metaldehyde Ratio (%)
1	580	38	7
3	360	11	3
4	160	4	2.5

A study of the persistence of metaldehyde in an analytical standard during method development experiments suggested that metaldehyde is a relatively stable compound under cold and anaerobic conditions (EA, 2009). This suggests that metaldehyde that has been potentially synthesised/produced *in situ* can potentially accumulate in the environment. If the metaldehyde was to be synthesised primarily within the landfill cell, percolating rainwater would cause the metaldehyde to leach into the aquifer. In a period of little to no rainfall, the metaldehyde concentration in the landfill cell could be expected to increase due to limited 'rinsing' by rainwater, therefore giving higher metaldehyde concentrations in the aquifer when rain does finally fall and percolate through the cell.

3.6 Proposed *in situ* mechanism

In order to assess the feasibility of an in-situ reaction, it is necessary to understand the mechanisms of the metaldehyde synthesis on a molecular level. No information is available on the reaction of four acetaldehyde molecules to form a metaldehyde molecule; however this section of the literature review illustrates a likely mechanism based on the evidence of similar reactions.

The organic mechanism of the cyclisation of acetaldehyde can be assumed from the very similar (albeit smaller and more reactive) compound formaldehyde. The chemistry of formaldehyde has been studied in more depth compared to acetaldehyde and it can be assumed that their reaction

mechanisms are somewhat similar due to the similarities between the two compounds (Figure 2). Formaldehyde and acetaldehyde share the same functional aldehyde group (reaction site) however acetaldehyde contains an extra CH_3 group instead of the smaller H.

Formaldehyde **Acetaldehyde**

Figure 2: Formaldehyde and Acetaldehyde

When in aqueous solution, the high reactivity of formaldehyde favours equilibrium with the water molecules to form its hydrate (Figure 3; based on Greeves et al., 2006).

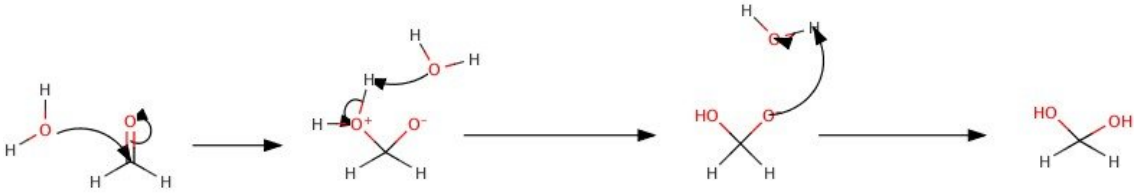


Figure 3: The reaction of formaldehyde to form the hydrate

The equilibrium constant (Kc) for this reaction is 2000, which means that essentially all of the formaldehyde in solution is present in its hydrated form (>99%) (Denver University, 2013). The same mechanism can be applied to acetaldehyde (Figure 4).

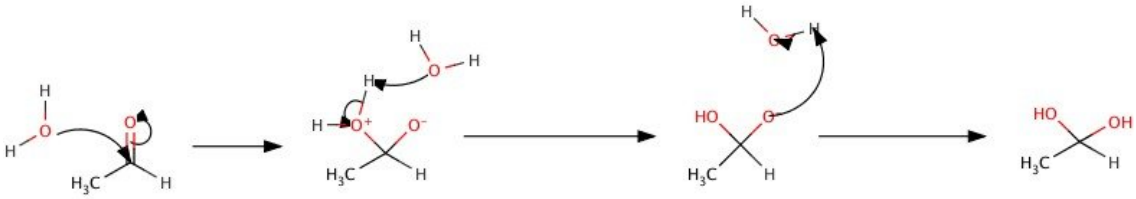


Figure 4: The reaction of acetaldehyde to form the hydrate

The equilibrium constant for the formation of the acetaldehyde hydrate is 1.3. This means that the reaction does not progress as far as formaldehyde and therefore more of the acetaldehyde is present in its non-hydrated form, approximately 50% compared to 99% for formaldehyde hydrate. However, this number is still relatively high when compared to other carbonyl compounds such as acetone, which has an equilibrium constant of 0.002 for this reaction (Denver University, 2013).

In the case of formaldehyde, the presence of acid catalysts can cause these 'activated' hydrate compounds to polymerise (Figure 5; Greeves et al, 2006)

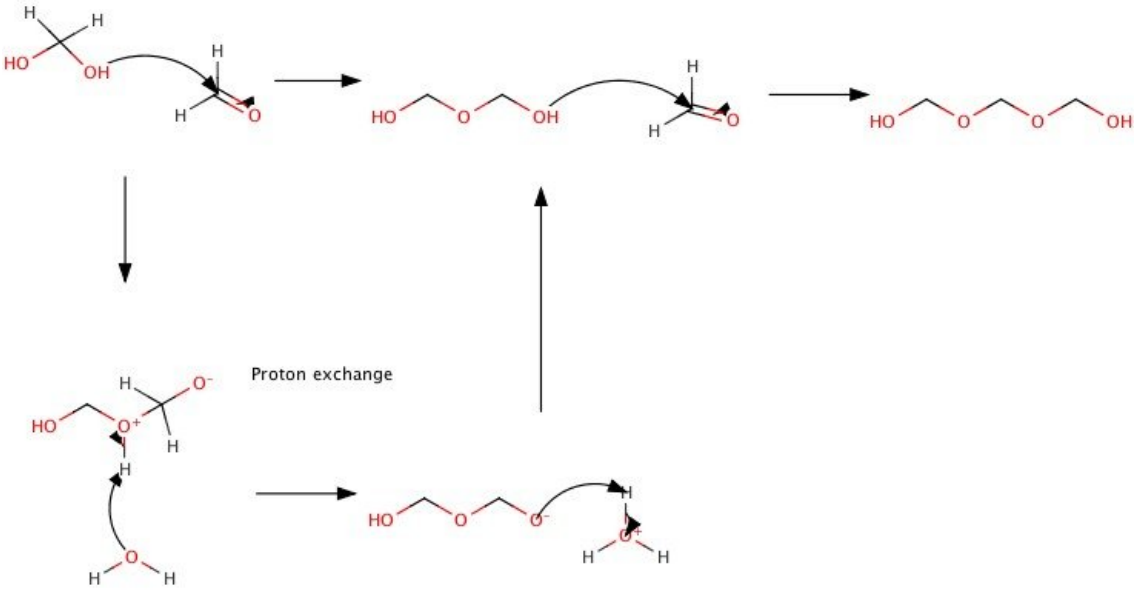


Figure 5: The reaction of the hydrated formaldehyde with itself to form a polymeric chain

Theoretically, this sequence of chemical reactions can continue indefinitely (with increasingly unstable products). However, many of the chains will close in on themselves to form the stable 1,3,5 – Trioxane. The favourability of this product is likely due to the low-strain 6-membered ring structure, which is commonly observed in compounds such as cyclohexane. Carbon atoms have their lowest energy when bond angles are arranged in a tetrahedron (109°) – therefore much of the reaction mixture will settle in this energetically favourable form, rather than creating unstable long chains or larger rings, shown in Figure 6.

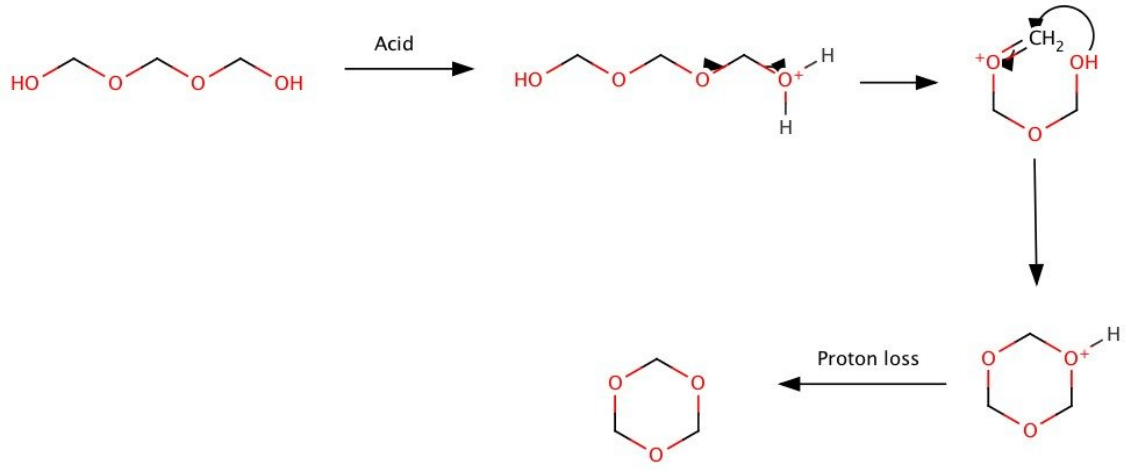


Figure 6: The ring closure reaction of the formaldehyde polymer to form the stable 1, 3, 5 - Trioxane

This cyclised product of formaldehyde is very similar in structure to paraldehyde. If this mechanism is applied using acetaldehyde as a reagent, paraldehyde is formed (and metaldehyde in smaller amounts) (Figure 7).

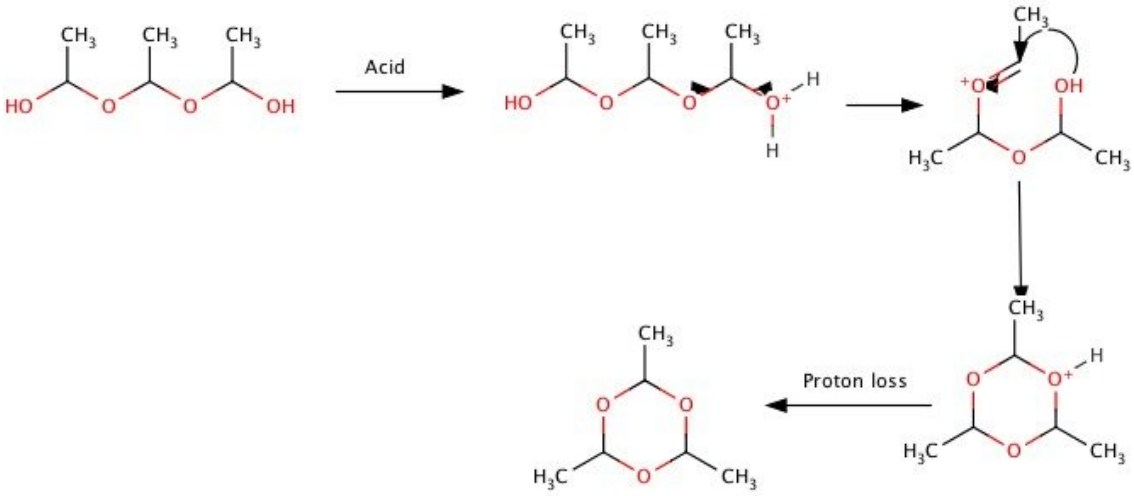


Figure 7: The ring closure reaction of the acetaldehyde polymer to form the stable paraldehyde

The formation of paraldehyde will also be favoured as all of the bond angles are in their most stable, lowest energy form. The formation of metaldehyde requires that the chain building reaction continues for another step prior to the ring closure. This forms a less favourable product as the bond angles are greater than 109° and places more strain on the bond angles in the ring. This explains why low yields are experienced during metaldehyde production. The complete proposed reaction mechanism for metaldehyde from acetaldehyde is detailed in Figure 8.

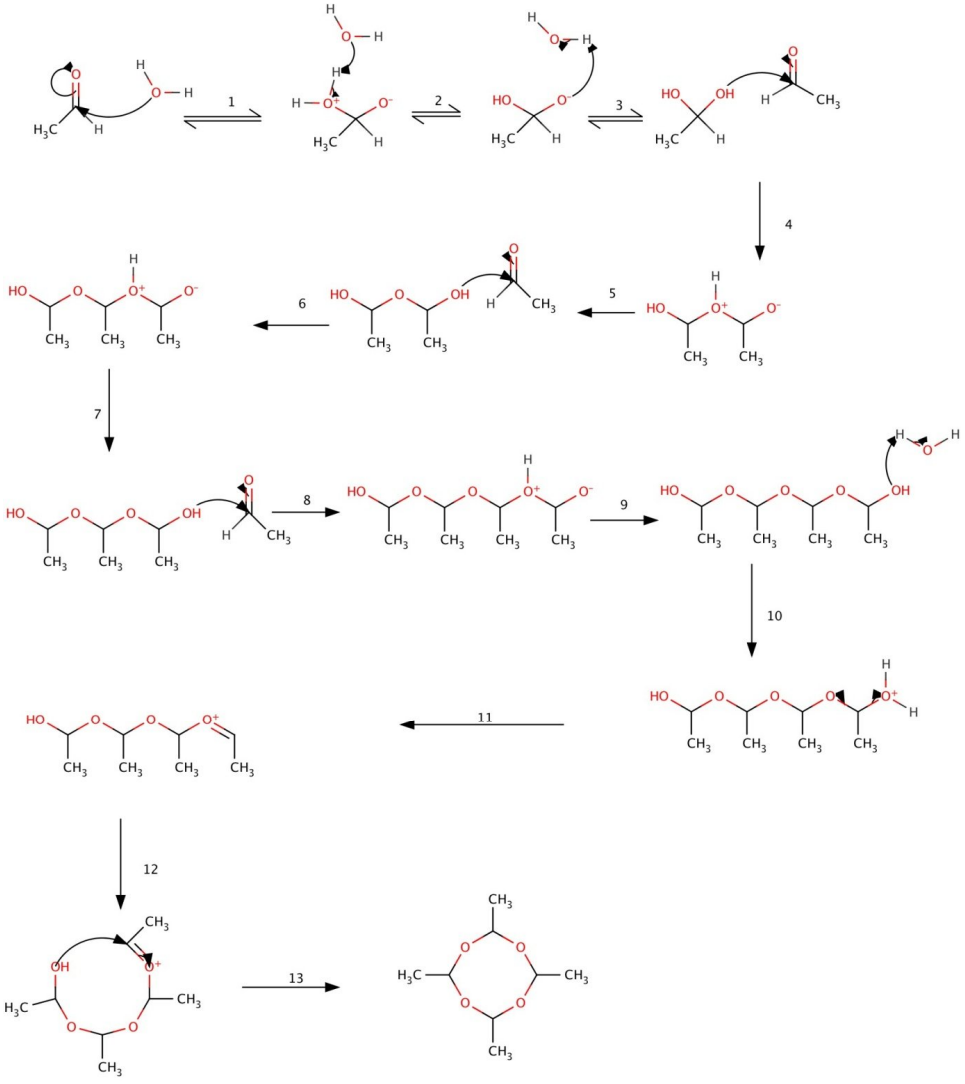


Figure 8: The complete proposed organic mechanism for *in situ* metaldehyde synthesis

The sequence of metaldehyde synthesis follows the sequence of:

1: The lone pair in the water attacks the aldehyde carbon, pushing the negative charge onto the carbonyl oxygen

2: The additional proton is removed from the positively charged oxygen…

3: …and transferred to the negatively charged oxygen, forming the hydrate of the aldehyde.

4: The alcohol group on either end of the newly formed hydrate then attacks the carbonyl carbon on an un-hydrated aldehyde molecule, pushing the negative charge onto the oxygen.

5: Protons are transferred as in steps 2 and 3

6. This process is then repeated through to step 8.

10. After the proton has been transferred in step 9, the alcohol group is acidified.

11. The lone pair from the oxygen in the chain pushes onto the unstable oxygen at the end of the chain, causing the end of the chain to leave as water. This forms an unstable double bond at the end of the chain.

12. The unstable intermediate.

13. The lone pair from the opposite end of the chain gives electrons to the other end of the chain and forms a closed ring.

3.7 Sources of reagents

From the proposed mechanism, the presence of acetaldehyde is the most important factor in forming metaldehyde *in situ*. Acetaldehyde is a key compound in many biological processes, meaning that there are likely to be multiple sources of this compound in the landfill environment, such as from partially combusted fuel (CEPA, 1993) and many food products, including dairy and fruit juices (Sellgren, 2013). Acetaldehyde is a product of the

microbiological conversion of ethanol, and the anaerobic conditions of the landfill sites have the potential to cause the formation of alcohols as the organic waste degrades.

Under oxidising conditions, this acetaldehyde can be converted to the carboxylic acid form, namely acetic acid. Acetic acid is commonly observed in leachates from landfills which are in their early acetogenic phase (Fang et al, 2012). As this oxygen supply diminishes over time, the ethanol will become less oxidised and acetaldehyde will accumulate. Though acetaldehyde has not been commonly monitored in landfill leachates, most likely due to the troublesome analytical method required to measure it, the study by Fang et al (2012) is one example where it has been measured. Acetaldehyde concentrations in the air were observed between 7.7 and 69 μg m^{-3}. The highest levels were observed around the gas extraction of a closed area of the landfill site. This suggests that the acetaldehyde is being produced in the anaerobic area of the landfill site where most of the fermentation will be taking place. Half of this level was observed at a sludge disposal workplace and at an active tipping site. This shows that acetaldehyde is present throughout the disposal process. Acetic acid (oxidised acetaldehyde) levels were found to be lower at the gas extraction vents and higher at the active tipping site. This supports the theory that areas with more oxidising conditions produce more acetic acid. The anaerobic conditions experienced at the source of the extraction vents will promote the formation of the less oxidised acetaldehyde and methane. From relative age of the landfill sites under study in this project (20 – 40 years), it can be assumed that conditions will be primarily anaerobic, supporting the possibility for a viable *in situ* formation mechanism for metaldehyde.

3.8 Conclusions

This critical review has shown that although the chemistry of landfill leachates and the chemical change through various landfill phases has historically been well characterised, very little published data exists on emerging organic contaminants and micropollutants. This is most likely because the sensitive

analytical methods have only been recently developed, and because the prevalence of these compounds in ground, surface and drinking waters has only been revealed recently. The legislative drivers from the WFD and DWD and the industry-independent body DWI will have also played in role in encouraging the collection of data on ground and drinking water contamination to take place, where it may not have otherwise been carried out. The collection of new data on metaldehyde concentrations in aquifers water will therefore provide useful information for future projects in assessing the sources, fate and pathways of micropollutants in the UK, particularly where landfill sites are believed to be a source of the micropollutants.

The review has demonstrated that an *in situ* synthesis of metaldehyde is feasible with landfill sites acting as potential sources of the conditions, reagents and catalysts necessary for its formation. Though no published data on the organic mechanism for metaldehyde synthesis was found, a realistic mechanism was able to be postulated using well-established organic chemistry literature. Knowledge of the required industrial conditions and the necessary landfill environment will enable lab-scale testing to be performed in order to simulate landfill conditions and determine whether the reaction is feasible in practice. If it is found that metaldehyde has the potential to be synthesised naturally in the environment, it could have significant impact on the future treatment of this compound with regards to legislation, environmental protection and water treatment processes. It would also provide grounds for further research investigating the kinetics of the reaction and finding ways of limiting its production in landfill sites. If the project shows no evidence of potential *in situ* synthesis, it will enable new investigations into point-sources of metaldehyde to be pursued and for remediation projects to be approached with more confidence, knowing that the metaldehyde is from a point-source.

4 Case Studies – Sites of Investigation

Initial investigations have taken place at two landfill sites located in the UK, which have shown evidence that the landfill sites are causing raised levels of metaldehyde contamination in the surrounding aquifers. The metaldehyde levels observed at pumping stations close to the sites have often exceeded the 0.1 µg L^{-1} limit set by the WFD. Further investigation will therefore be carried out at these sites to provide further evidence as to whether the landfill sites are a point-source of metaldehyde, or whether the metaldehyde is present in the groundwater for different reasons such as agricultural applications.

4.1 Study Areas

4.1.1 Helpston

Located in the Anglian Water region of the UK, the Helpston area (Figure 9) was initially investigated because of high levels of Mecroprop contamination. Contamination was found in the Lincolnshire Limestone, Grantham Formation and Northampton Sands aquifers (Figure 10) surrounding two landfill sites constructed in the 1980s and closed in the 1990s, Ailsworth Road and Ben Johnsons Pit. Both sites have a combined area of approximately 0.6 km^2. In 2008, it emerged that metaldehyde had also been detected at a pumping station within the area, and later investigations by the Environment Agency concluded that the closed landfill sites were a possible source of the observed contamination.

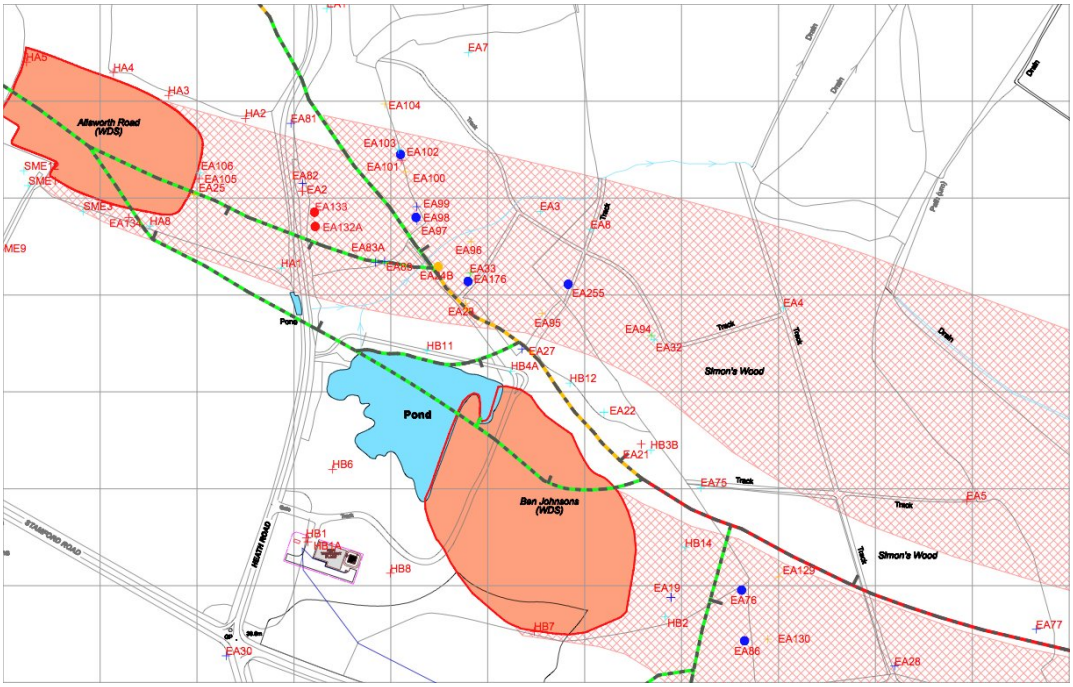


Figure 9: Map showing the Helpston area with borehole locations and the proposed contaminant plume (the theorised plume is indicated by the red cross-hatched areas emerging from the east side of each pit). 1 grid square = 100 m^2.

Since these initial investigations, significant work has been carried out at both pits, including further investigations into the contaminant levels and remediation works such as groundwater treatment and *in situ* aeration. An investigation carried out and reported in 2013 by environmental consultants concluded that there were two contaminant pathways leading from the site and that both of the closed sites were a potential source of the contamination. Correlation between metaldehyde and mecoprop was found to be positive enough to conclude that both landfill sites were a likely point-source of metaldehyde and mecoprop.

The study also found that metaldehyde concentrations were closely related to the groundwater levels, to the extent that metaldehyde concentrations could be predicted prior to testing with good accuracy. Whilst this provides further evidence that the contamination is not from agricultural run-off, this finding also suggests that the metaldehyde release from the landfill site is constant, and that

lower observed concentrations are likely due to dilution by uncontaminated groundwater.

Current remediation work at the site involves abstracting contaminated groundwater using a number of pumps connected to a central manifold. Water is then treated using a variety of techniques and discharged into a nearby pond.

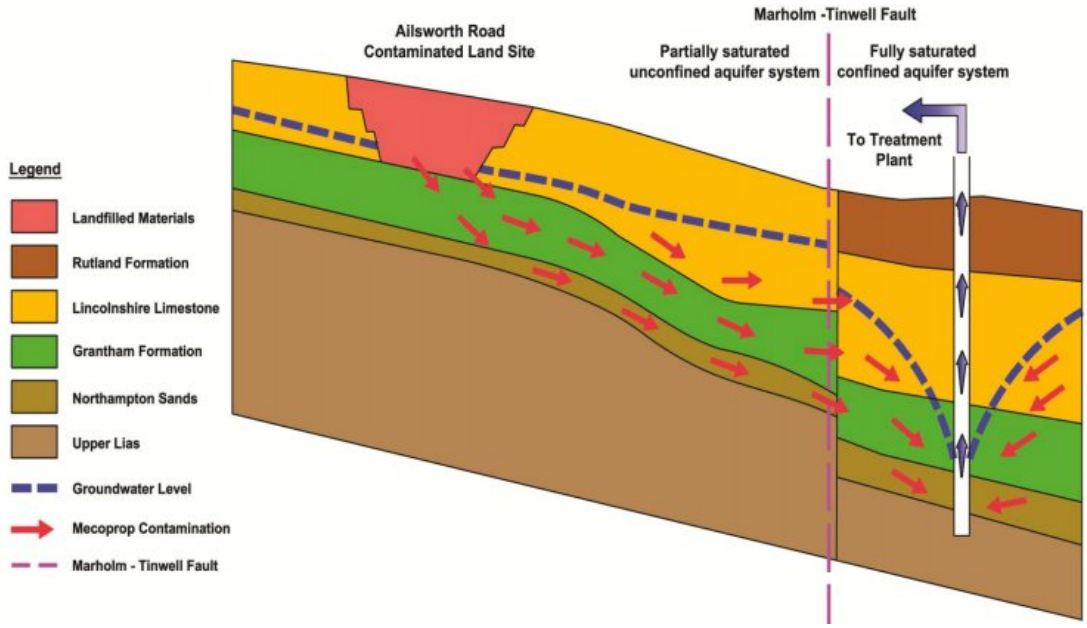


Figure 10: Hydrogeology of the Helpston area (reproduced from Cooper and Warrington, 2013)

4.1.2 Smallford

Located in the Affinity Water region of the UK, the Smallford landfill site (Figure 11) was constructed in the 1960s and closed towards the end of the 1970s. This case is more of an emerging problem compared to the Helpston site as the metaldehyde problem was discovered in the last couple of years when raw water sources downstream of the landfill site were found to exceed the metaldehyde limits for drinking water. The site is public amenity land and had had no remediation or further study at the start of this project. However, since the start of this project, the Environment Agency and other contractors have carried out their own investigations.

The existing data from the water company shows metaldehyde concentrations are greater downstream of the landfill site. Though some study of the hydrogeology of the site has taken place (establishing a northwest-southeast aquifer flow), little is known about the depth of the landfill site or the nature of the waste contained within it.

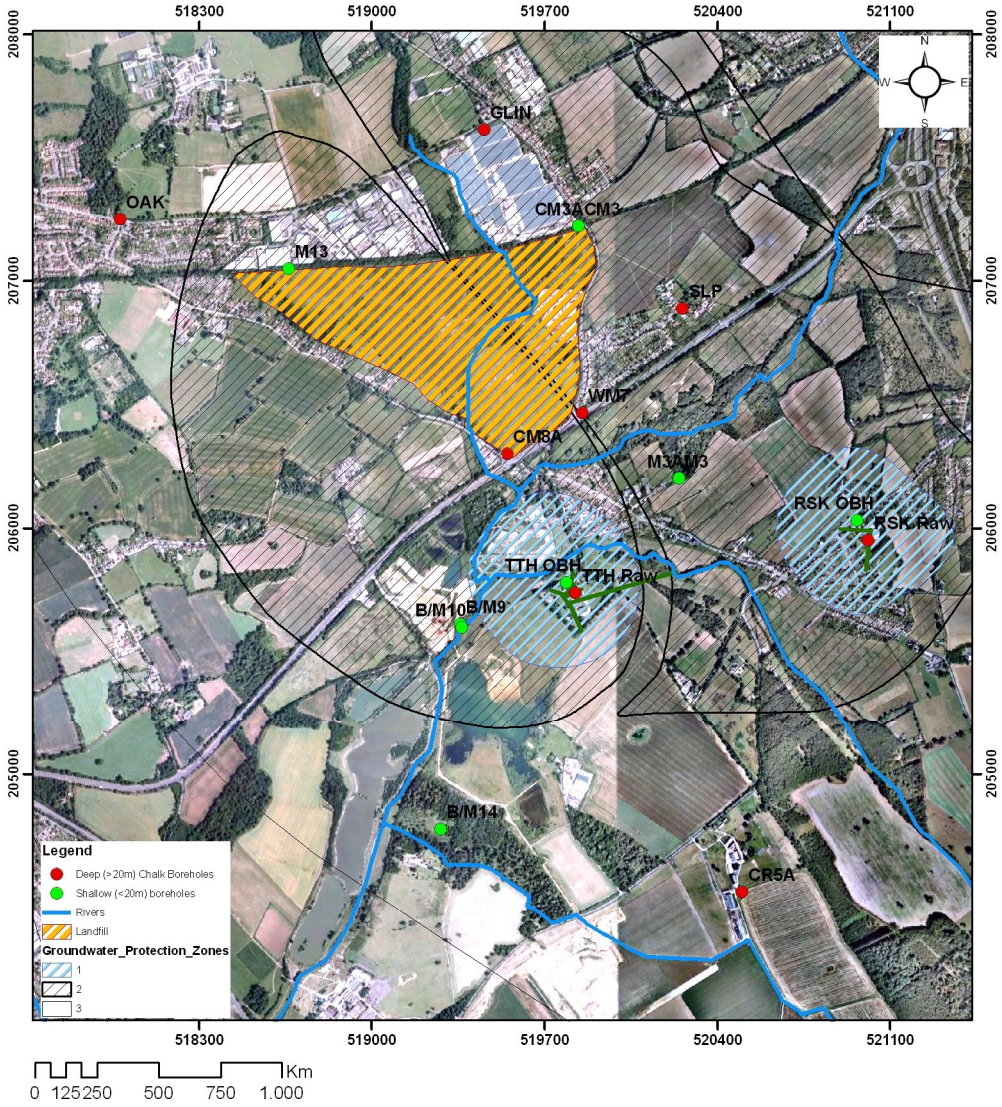


Figure 11: Map of the Smallford area showing borehole locations

4.2 Methodology

Routine sampling was carried out over a seven month period at both sites. The same approach to groundwater sampling could not be used at both sites, this was due to major differences between the work already carried out at each location. For example, the Helpston landfill has had significant remedial work carried out over recent years, and as a result has a much greater number of observation boreholes in and around the contaminant plume. Some boreholes also actively pump out groundwater for treatment, meaning that boreholes are constantly purged and do not require the use of a separate pump for sampling Conversely, the Smallford site has not had any remedial work carried out, and has a very limited number of boreholes available for sampling. However all samples were analysed using the same analytical method of solid phase extraction followed by Gas Chromatography analysis with Mass Spectrometry detection (GC-MS).

4.2.2 Helpston Landfill

The extent of groundwater contamination at the site was monitored by sampling the abstraction pumps used for site remediation. Whilst they were mainly chosen for being the safest areas to sample from, these boreholes were also strategically placed in the established contaminant pathways by the environmental consultants and are most likely to have higher metaldehyde concentrations than other boreholes. Samples were also taken from pathways further along the established contaminant pathways in conjunction with a project carried out by the Environment Agency which continuously monitors the extent of the Mecoprop contamination in the groundwater

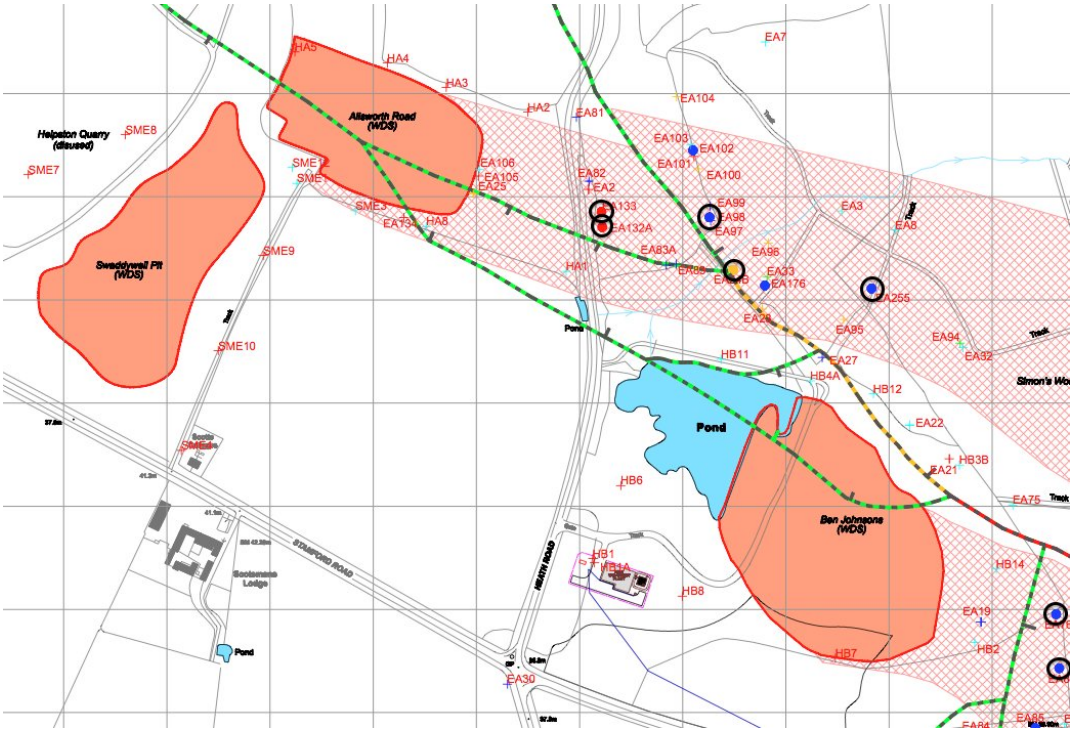


Figure 12: Map showing the most frequently sampled boreholes (circled in black). These were amongst the boreholes which actively pumped water for remediation.

For the majority of samples at this site, water could be abstracted using pumps that were already actively pumping water. Some of these samples could be taken directly above the pump by the connection of a hose or from the central manifold, prior to where all pumped water is combined and subsequently treated (these points are highlighted in Figure 12). Other samples, which were further away from the landfills and outside the remediation area, were sampled using a variety of electronic pumps.

As the metaldehyde concentrations of the samples at this site ranged from 0.1 to over 100 µg L^{-1}, analysis was made more problematic as a reasonable calibration range could not be used. Though this could be solved by introducing standards of a higher concentration to the calibration, having a calibration range which was too large affected the sensitivity of the lower concentrations. The large concentration ranges were often observed between samples from the same sampling point, so predicting the necessary dilution required was not

possible. Therefore, the maximum concentration that could be calculated in a one-time routine analysis was 50 µg L^{-1}.

4.2.3 Smallford landfill

Boreholes at this site were monitored mainly via observation boreholes, which have been installed around the perimeter of the affected site and downstream of the suspected contaminant pathway. As the metaldehyde problem has only recently surfaced, most samples could only be taken from pre-existing boreholes, and were therefore not as strategically placed along the proposed contaminant plumes.

Three of the sampling points are known to enter a deeper chalk aquifer (Glinwell, WM7 and CM8A, see Figure 13). Other boreholes are known to be abstracting from shallower clay and gravel layers. During this project, some leachate wells were drilled on the surface of the landfill site to a depth of 8-12 meters, some of which were also included in this study (L3 and L5). Whilst the small number of boreholes is a limitation to this study, a mix of deep and shallow boreholes allows the link between the hydrogeology and contamination to be assessed. Rainfall data is also available at this site, which will allow the relationship between the degree of contamination and rainfall to be addressed. A description of the approximate depth and location of each sampling point is summarised in results section.

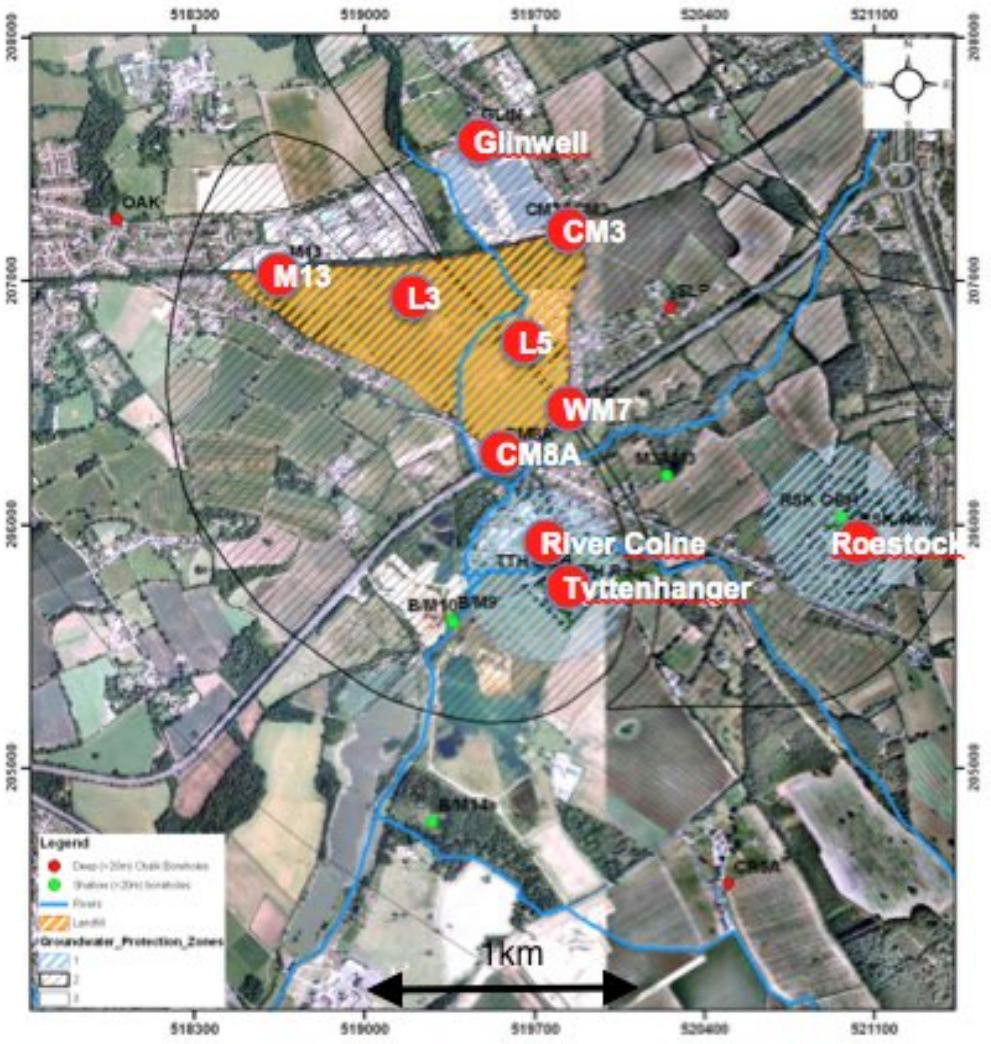


Figure 13: Map showing the location of each sampling point at Smallford.

4.2.4 Analytical method

The method used for the detection of metaldehyde was based on Method A from the Environment Agency's methods for the examination of waters and associated materials (Environment Agency, 2009). Metaldehyde was extracted from 250 ml water using solid phase extraction cartridges recommended and supplied by Phenomenex. For the majority of the project, Strata SDB-L Styrene Divinylbenzene polymer cartridges were used, as per the method. However, due to unavoidable supply issues, samples analysed after February 2014 were

extracted using Strata-X 33u Polymeric Reversed Phase cartridges. Discussions with Phenomenex concluded that this would have no negative effect on the extraction efficiency or the recovery of metaldehyde from the cartridge. This was because the solid phase had similar polar interactions with the metaldehyde and the larger surface area of these cartridges theoretically allowed more loading of sample. The only notable difference was a slower extraction due to a more densely packed column.

When this method was developed in 2009, deuterated metaldehyde for use as an internal standard was not available for purchase. Since this time, a d_{16}-metaldehyde standard has been developed commercially by QMX, and this was used based on expert advice from discussions with water companies and the latest analytical methods being developed at the time. The use of this internal standard also ensured that any slight differences in the adsorbing properties of the new columns were accounted for as the ratios of analyte to internal standard would remain constant.

To account for the large concentrations often observed at the Helpston landfill sites, an extension of the calibration range was also required to adequately quantify the samples. Calibration standards of 0.05, 0.1, 0.2, 0.5, and 1 mg L^{-1} were used as a standard procedure, with calibration standards of 2, 5, 10 and 20 mg L^{-1} being used where higher levels were found. Samples were run using Selective Ion Monitoring (SIM) detection to specifically target metaldehyde and the d_{16}-metaldehyde internal standard. Ultra-pure water used during the analysis was analysed using the same method as the samples and was found not to contain metaldehyde in any instance.

Triplicate analysis of identical samples analysed through the project are shown in Table 7 to demonstrate the repeatability of the method at different metaldehyde concentrations. The repeatability of the extraction was generally very good, as shown by the similarity between the replicate solvent extracts. The average standard deviation between the replicate samples was 0.035 mg L^{-1}, giving an uncertainty of ± 0.1 ug L^{-1} in the final calculation of a 250ml water sample.

Table 7: Results showing the concentrations of the dichloromethane extract from 250ml aqueous samples

Sample	Metaldehyde concentration of solvent extract (mg L^{-1})
A (From a diluted acetaldehyde solution)	0.01
	0.01
	0.01
B (From a diluted acetaldehyde solution)	1.48
	1.50
	1.54
C (From an acidified diluted acetaldehyde solution)	2.39
	2.31
	2.33
D (From an diluted acetaldehyde solution adjusted to pH 7)	3.12
	3.06
	3.06

4.3 Results and discussion

4.3.1 Helpston landfill site

Full results for the monitoring of metaldehyde levels for boreholes which were routinely sampled are summarised in Table 8. Other boreholes sampled less

routinely are summarised in Table 9. Figures 14 and 15 show maps of the area with the sampling locations highlighted.

Table 8: Metaldehyde results for routinely sampled boreholes. Descriptions of their location are given in relation to Ben Johnson's Pit (BJP) and Ailsworth Road Pit (AWP)

	Metaldehyde concentration (µg L^{-1})						
	Sampling point						
Date sampled (dd/mm/yyyy)	**EA98**	**EA24B**	**EA133**	**EA255**	**EA132A**	**EA76**	**EA86**
18/10/2013	0.2	29.4	46.5	15.0	17.5	11.5	-
12/11/2013	12.5	17.8	30.8	4.6	-	6.9	> 50
11/12/2013	16.2	22.3	-	0.3	-	35.2	> 50
6/2/2014	0.1	0.1	0.2	n.d	-	0.2	19.9
14/3/2014	0.2	10.0	15.3	4.8	9.6	11.3	16.0
2/5/2014	8.4	17.0	42.8	13.3	> 50	9.1	12.5
Location	~250m E AWP	~300m E AWP	~150m E AWP	~400m E AWP	~150m E AWP	150m E BJP	150m E BJP

Table 9: Other Helpston boreholes, sampled less frequently. Descriptions of their location are given in relation to Ben Johnson's Pit (BJP) and Ailsworth Road Pit (AWP)

Sampling point	Date sampled (dd/mm/yyyy)	Metaldehyde concentration (µg L^{-1})	Location description BJP=Ben Johnson's Pit AWP = Ailsworth Road Pit
EA85	16/10/2013	34.1	~100m SE of BJP
EA16	22/10/2013	3.4	~2km E of BJP
SME2		0.6	~100 NW of AWP

Fox Covert		0.1	~5km NW of BJP
Werr Junc		1.7	~3km E of BJP
EA18		0.2	~2km NE of BJP
EA95		9.3	~100m N of BJP, ~400m E of AWP
EA32	23/10/2013	7.0	~100m NE of BJP, ~500m E of AWP
EA25		8.6	~100m N of BJP, ~300m E of AWP
EA97	24/10/2013	34.5	~200m N of BJP, ~250m E of AWP
EA3		3.7	~200m N of BJP, ~350m E of AWP
EA100		0.2	~200m N of BJP, ~200m E of AWP
EA2	25/10/2013	> 50	~300m NW of BJP, ~100m E of AWP
EA77		0.6	400m east of BJP, N side of faultline
EA9		8.9	~1km NE of BJP
Stream	10/12/2013	0.1	Unspecified
EA23		5.3	~100m N of BJP, ~300m E of AWP
EA79		0.6	~3km SE of BJP
HB12		0.9	~50m N of BJP
HB3B		2.1	~50m NE of BJP
HB14	11/12/2013	7.4	~50m E of BJP
HB2		18.0	~50m SE of BJP
EA10		9.1	~800m SE of BJP
EA28		15.9	~300m SE of BJP
Heath Road	12/12/2013	0.05	~50m E of BJP

EA129		4.4	~150m E of BJP
EA130		43.0	~200m E of BJP
BJP Overflow		0.2	Pond directly W of BJP
EA16	15/01/2014	3.3	~2km E of BJP
EA95		8.8	~100m N of BJP, ~400m E of AWP
EA97		36.9	~200m N of BJP, ~250m E of AWP
EA18		0.05	~2km NE of BJP
EA9		5.5	~1km NE of BJP
Werr Junc		1.8	~3km E of BJP
EA96		2.8	~150m N of BJP, ~300m E of AWP
EA32	16/01/2014	2.3	~100m NE of BJP, ~500m E of AWP
EA100		3.3	~200m N of BJP, ~200m E of AWP
EA25		8.6	~100m N of BJP, ~300m E of AWP
EA3		3.5	~200m N of BJP, ~350m E of AWP
EA2	20/01/2014	15.0	~300m NW of BJP, ~100m E of AWP

Figure 14: Map of Helpston with sampled borehole highlighted (1 grid square = 100m^2)

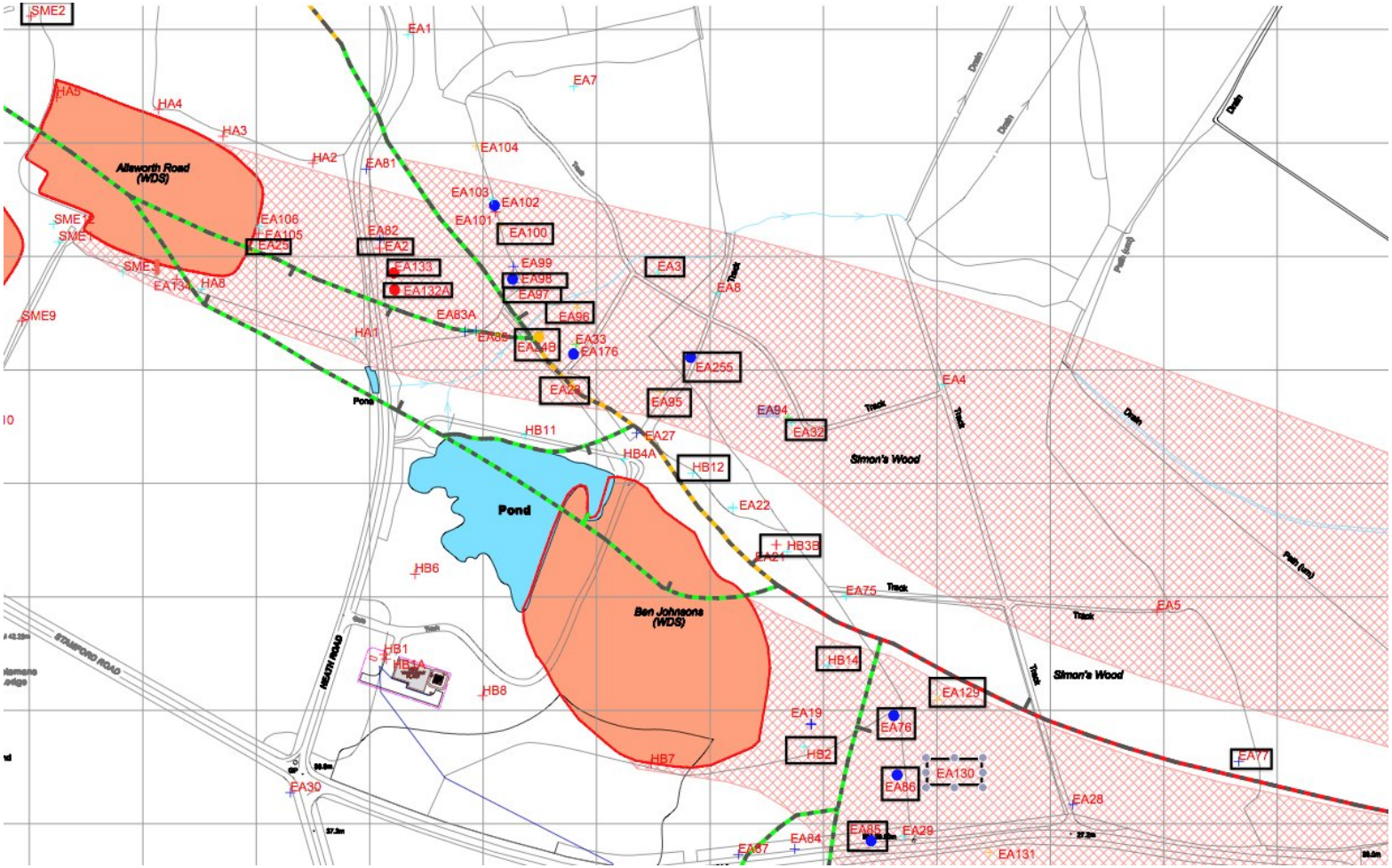
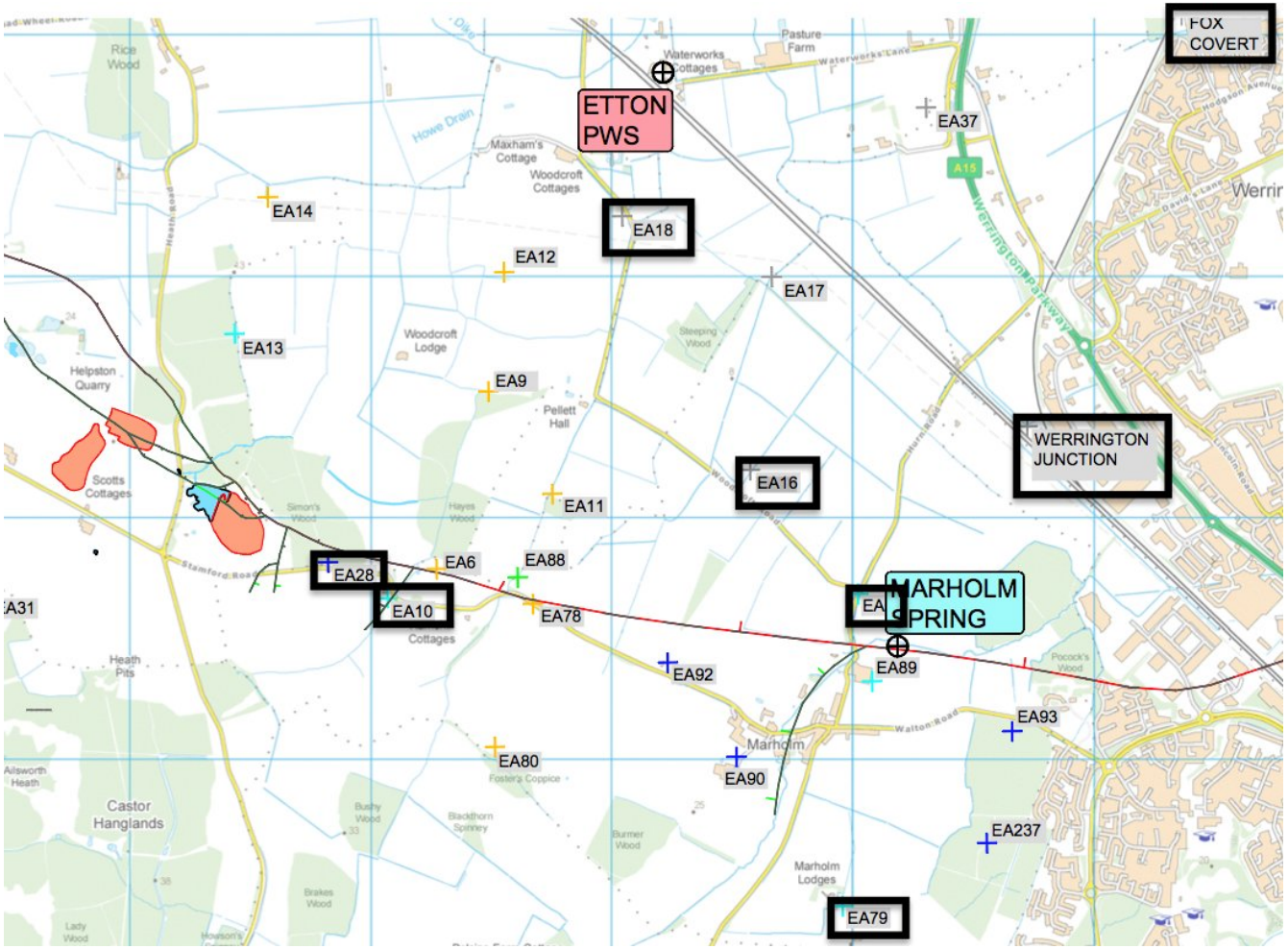


Figure 15: Larger scale view of the Helpston area, with more distant sampled boreholes highlighted (1 grid square = 1km^2)



The data supports the findings of the studies carried out by the Environment Agency and the consultants that the landfill is a point source of the metaldehyde contamination.

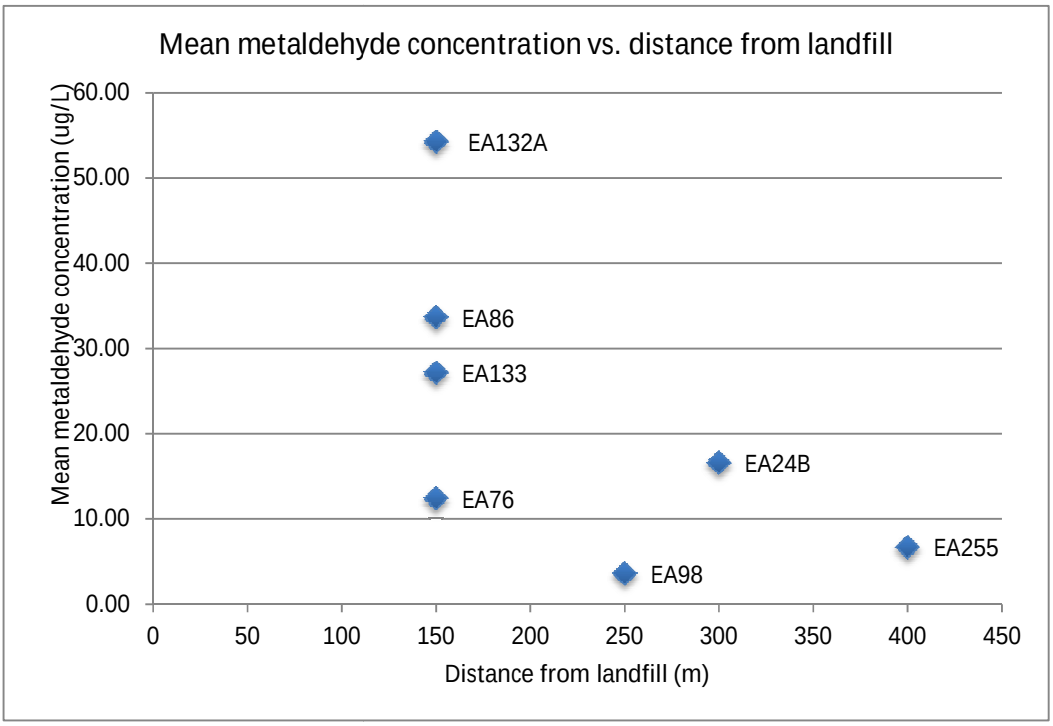


Figure 16: A demonstration of the lower contaminant concentrations observed at sampling points located further from the landfill site

As shown in Figure 16, with the exception of EA132A, lower concentrations are generally observed in boreholes which are further away from the landfill sites, as shown in the study by Baziene et al (2013) This is likely to be due to mixing with uncontaminated groundwater as the plume spreads eastwards. EA133, located directly east of the Ailsworth Road pit shows some of the highest concentrations with a mean concentration of 27.7 µg L^{-1}. EA24B (located approx. 100 m further east) and EA255 (located a further 150 m) show

progressively lower values, with mean concentrations of 16.1 µg L^{-1} and 6.3 µg L^{-1} respectively. Similar fluctuations in concentrations can also be observed from the plotted data in Figure 17. Concentrations are generally higher around October-November, with a lowering in concentration towards January. Levels are then found to rise again as 2014 progresses. This therefore suggests that the concentrations in boreholes is controlled by a single factor such as groundwater levels, highlighted in the previous studies. The decline in metaldehyde concentrations during the colder months may also be due to the cold temperatures inhibiting the mobility of the contaminants as less dissolution may occur. Colder temperatures would impede the rate at which contaminants dissolve into the water, so rainfall that percolates through the waste could potentially accumulate less contamination before it is released into the aquifer.

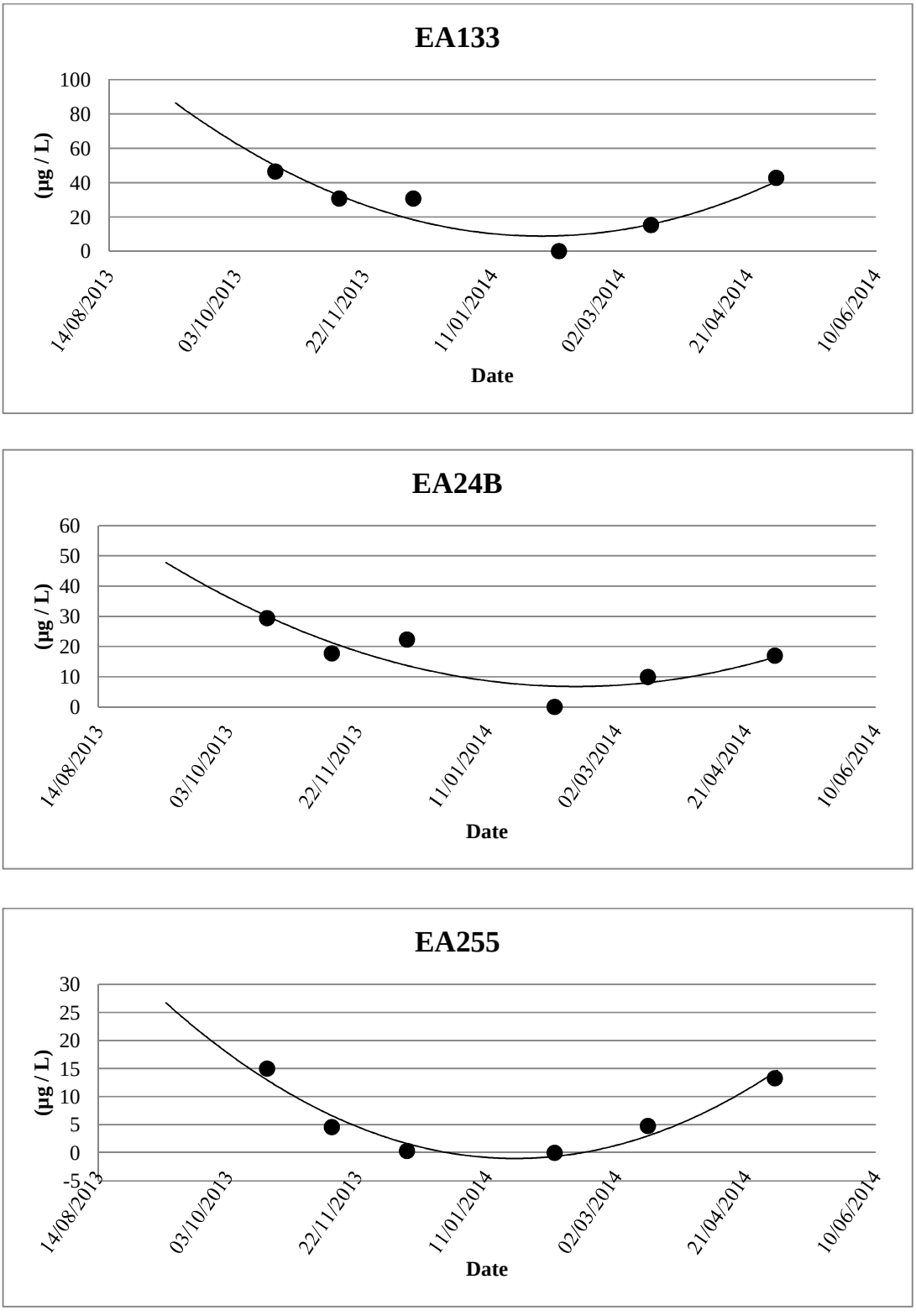


Figure 17: Metaldehyde concentrations at boreholes EA133, EA24B and EA255

In addition to this, boreholes which are located significantly further away show much lower metaldehyde concentrations. EA16 and EA79, which are located 2-3 km east of the site, were found to contain 3.3 µg L^{-1} and 0.6 µg L^{-1} respectively.

However, some exceptions to this rule are observed when sets of samples collected within the same week and area are looked at together (Figure 18).

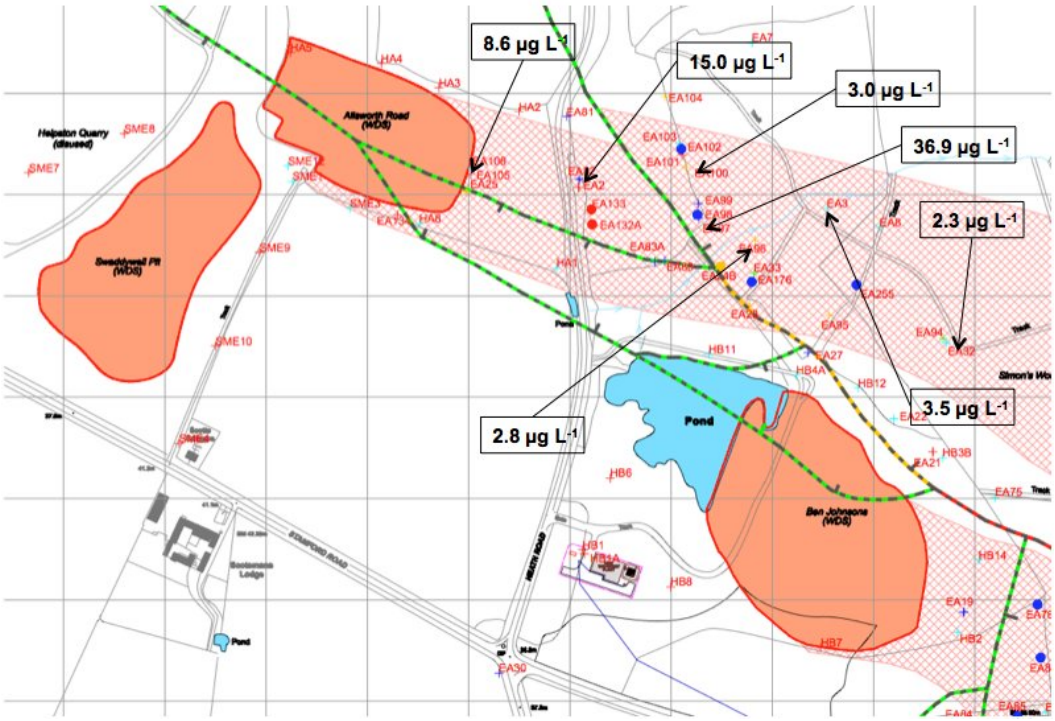


Figure 18: Map showing the concentrations of metaldehyde found in various boreholes in the same week at Helpston

In this instance, large differences in contaminant concentration can be observed between boreholes within close proximity to one another. This can suggest that metaldehyde may have preferential pathways through the aquifer. This could be due to adsorption to solid mediums within the aquifer, be it waste in the landfill, the limestone or sand. Pathways may also become more complex as the contamination moves around the geographical faults. The position of these faults is shown as the green, yellow and red dashed lines on the maps.

The fact that a lower concentration is observed directly next to the landfill site suggests that if the landfill is a point-source of metaldehyde, the contamination point is discrete and is not homogenous throughout the whole of the landfill. The majority of the contamination may therefore by-pass this borehole, and flow more directly to other boreholes.

Preferential contaminant can also be caused by the differences in the hydraulic properties of the solid waste in different layers. Older waste, which is more likely to be found at the base of the landfill, will be at a more advanced phase of decomposition; This causes the waste to be more densely packed due to greater compaction and have a finer particle size (Wu et al, 2012 and Reddy et al (2011)). Conversely, fresher waste situated towards the top of the landfill has had less time to decompose, is not packed as densely and has larger particle sizes. The study by Wu et al (2012) showed that older, finer waste can hold significantly more water than fresher waste (and therefore more dissolved contaminants). This highlights that percolating rainfall is unlikely to penetrate the entire landfill before entering the groundwater, and in some cases may leach out at shallower depths where the hydraulic flow is more favourable. The limited leachate flushing properties exhibited by older, more compacted waste could also indicate that metaldehyde which has percolated through to deeper layers is first retained, and then steadily released into the aquifer when more significant flushing occurs. This could explain the close link which metaldehyde has with groundwater levels at this site, as a steady and constant release of contamination from the retentive waste would give higher concentrations during low groundwater periods, and lower concentrations during higher groundwater periods.

The active abstraction at this site must also be taken into consideration as this will cause zones of depression in the water table and affect the natural flow of the aquifer. As the contamination is abstracted from the plume, an influx of uncontaminated water will flow in to replace it. Therefore, the unexpectedly low value of 3.0 μg L^{-1} observed at EA100 could be due to an influx of

uncontaminated groundwater caused by the abstraction at the nearby EA102 abstraction point.

The depth of the boreholes could also be a contributing factor to these differences, though sufficient data was not available for this to be investigated fully. Some boreholes may not penetrate deep enough into the groundwater to reach the contaminant plume, or conversely could be too far down past the contaminant plume. However if this was the case, it would be expected that one borehole would show consistently lower values than an adjacent borehole. For example, EA98 and EA24B are both located less than 100 m from one other, and significant differences were observed in their metaldehyde concentrations in October 2013 (0.2 µg L^{-1} and 29.4 µg L^{-1} respectively). If EA98 was not sufficiently abstracting contamination, a consistent concentration ratio between the two boreholes would be expected. However, the following month, the concentrations at EA24B dropped to 17.8 µg L^{-1} whilst concentrations at EA98 rose to 12.5 µg L^{-1}. This therefore suggests a change in the contaminant pathway rather than borehole depth being a significant factor in the concentration differences.

4.3.2 Smallford landfill site

All data on the metaldehyde concentrations at Smallford landfill site are summarised in Table 10. A map of the area showing the location of each sampling point is shown in Figure 19. A description of each sampling location in relation to the landfill site and their approximate depths are shown in Table 11. In some instances towards the end of the sampling period, leachate samples from newly drilled wells L5 and L3 were able to be collected. Borehole M13 is the most shallow borehole, and was often found to contain no groundwater, therefore less data is available for this sampling point.

Table 10: Metaldehyde concentrations from the Smallford area

	Metaldehyde concentration (µg L^{-1})									
	Sampling point									
Date sampled (dd/mm/yyyy)	**WM7**	**CM8A**	**CM3**	**M13**	**River Colne**	**Tyttenh-anger**	**Roest-ock**	**Glinwe-lls**	**L5**	**L3**
09/09/2013	3.0	0.6	0.1	-	0.3	-	-	-	-	-
08/10/2013	2.0	0.6	-	-	-	0.4	-	-	-	-
29/10/2013	-	-	-	-	0.8	0.5	0.3	-	-	-
19/11/2013	1.3	0.3	n.d	-	0.1	0.1	0.05	0.2	-	-
10/12/2013	1.4	0.3	n.d	-	0.05	0.2	0.05	0.1	-	-
14/01/2014	2.2	0.5	0.1	n.d	0.2	0.4	n.d	n.d	-	-
05/02/2014	1.8	0.6	1.5	n.d	1.3	0.9	0.2	0.3	-	0.5
25/02/2014	0.8	0.1	n.d	-	n.d	0.05	0.1	0.05	0.3	-
18/03/2014	1.2	0.2	0.05	-	n.d	0.1	0.05	n.d	0.1	-
30/04/2014	1.9	0.3	n.d	-	0.05	0.3	0.1	0.05	0.3	-

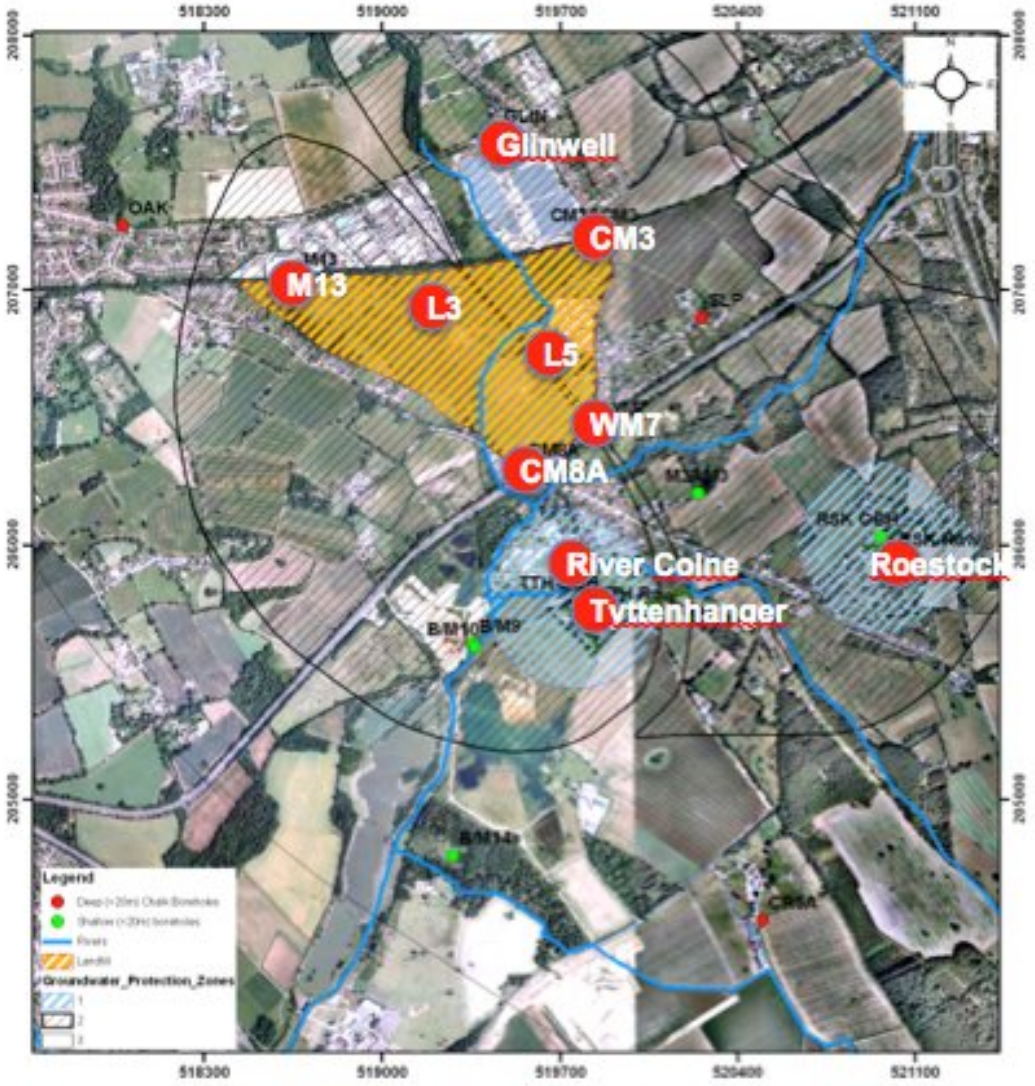


Figure 19: Map of the Smallford area, showing the location of the boreholes sampled

Table 11: A description of the location of each sampling point in relation to the landfill site and its approximate depth

Sampling point	Approximate depth (m)	Location
Glinwell	30 – 60 (chalk aquifer)	~300m north of landfill
CM3	12 (gravel aquifer)	On the northeast corner of the landfill
M13	8 (gravel aquifer)	On the northwest perimeter of the landfill
L3	12 (leachate well)	North-centre of the landfill
L5	12 (leachate well)	East-centre of the landfill
WM7	30 (chalk aquifer)	Southeast corner of the landfill
CM8A	30 (chalk aquifer)	~200m from WM7
River Colne	N/A (surface water)	~100m from Tyttenhanger entrance, ~500m south of landfill
Tyttenhanger	30 – 60 (chalk aquifer)	Pumping station located ~800m south of the landfill
Roestock	30 – 60 (chalk aquifer)	Pumping station located ~1500m southeast of the landfill

The new data (Table 10) supports the findings of previous investigations carried out by Affinity Water that the landfill is a contributing factor of the metaldehyde contamination and a likely point source. Boreholes to the south of the site which penetrate to the deeper chalk aquifer (WM7 and CM8A) were found to contain

significantly higher levels of metaldehyde than the chalk borehole located to the north of the site (Glinwells). This is consistent with the predicted northwest-southeast flow of the aquifer. Boreholes that are further away from the landfill, Tyttenhanger and Roestock, also show a decreased concentration most likely caused by mixing with uncontaminated groundwater. This trend is highlighted in Figure 20 for the chalk boreholes which abstract from the same aquifer. The Glinwell borehole was not included in the chart as this sampling point is located to the north of the landfill and would therefore not be part of the predicted contaminant plume.

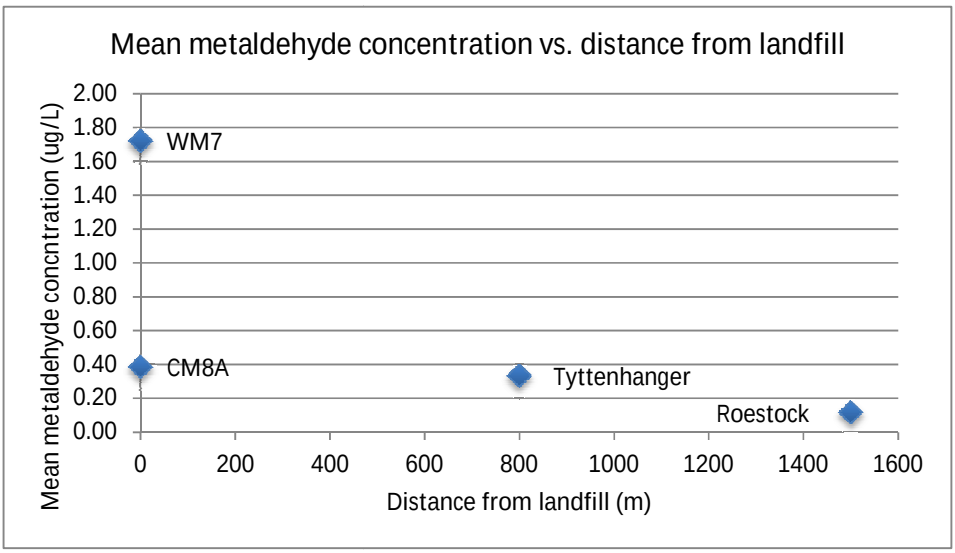


Figure 20: A demonstration of the lower contaminant concentrations observed at sampling points located further from the landfill site

Metaldehyde levels were generally found to be lower in the shallower boreholes which penetrate the clay or gravel layers (CM3 and M13). This suggests that most of the contamination was coming from the deeper layers of the landfill. This was supported by the unexpectedly low metaldehyde concentrations observed in the leachate wells, which were approximately 8-12 m deep. The metaldehyde concentrations in these wells were consistently lower than the chalk borehole WM7, suggesting that the wells have either not bored down deep enough to the source of the contamination, or have not located a discreet source of metaldehyde. Unfortunately, the lack of shallow boreholes located to

the south of the landfill also prevented the collection of further evidence to support that the contamination is limited to the lower chalk layers.

The hypothesis that the landfill was the point source of contamination was also supported by the difference in metaldehyde concentrations observed between the shallow boreholes M13 and CM3 and the newly drilled leachate wells. All four of these sampling points bore down to a similar depth, however the leachate well concentrations are consistently higher than the shallow boreholes, indicating that contamination at this depth can only be coming from the landfill site, and not from the water flowing from north of the landfill. This observation is particularly clear on the samples taken on the 5th of February 2014, as no metaldehyde was detected in borehole M13, but was detected in leachate well L3 located approximately 200m away. The plotted data can be observed in Figure 21.

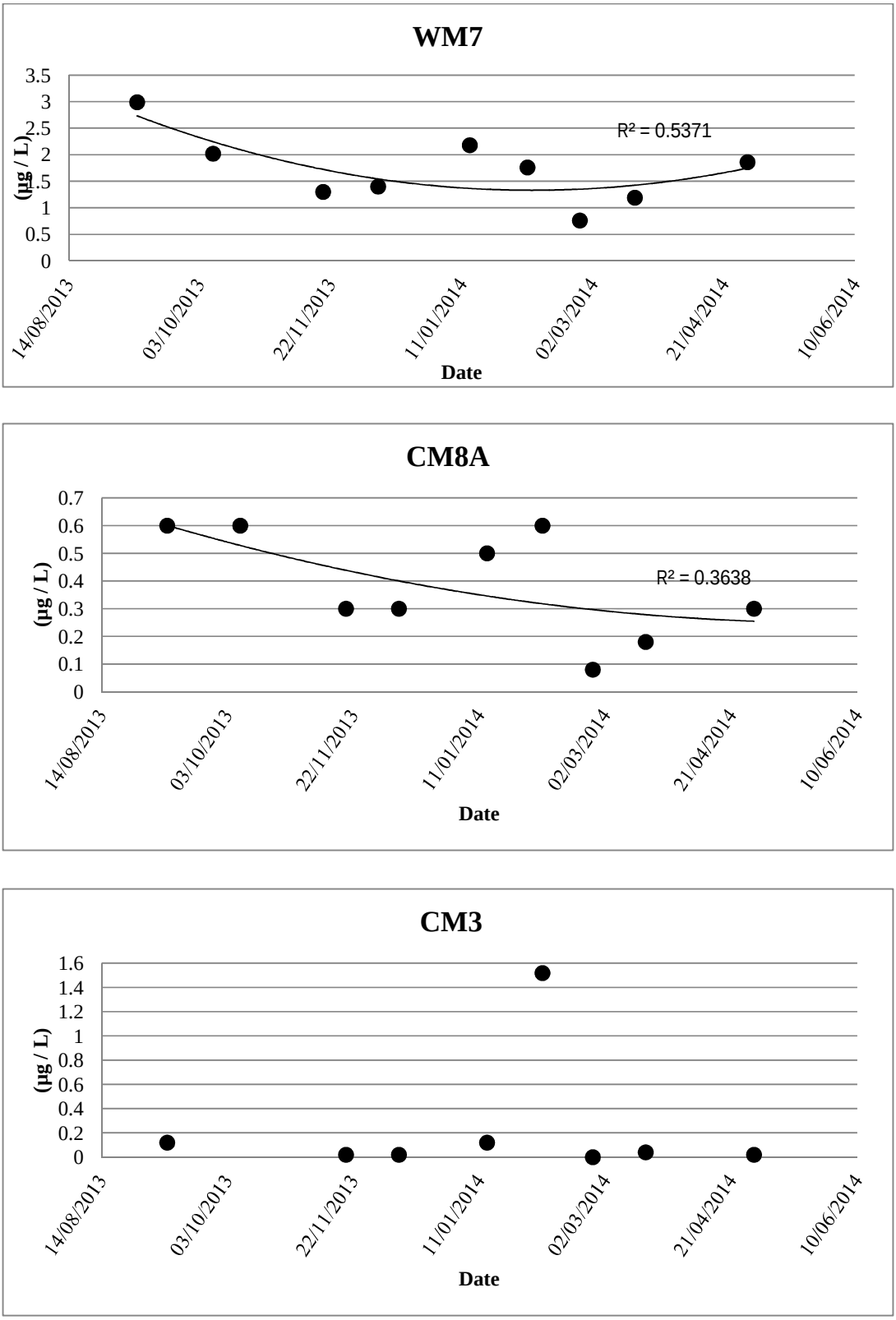


Figure 21: Metaldehyde concentrations at boreholes WM7, CM8A and CM3

A general trend was observed for the deeper chalk boreholes Glinwell, WM7 and CM8A; Metaldehyde concentrations at these points show peaks in concentration in September, January and April and lower concentrations in November and March. This suggests that the contaminant concentrations in the chalk aquifer share the same controlling factor, such as groundwater levels or rainfall. Different trends can be observed in shallow boreholes such as CM3, suggesting that there is little interaction between the deeper and the shallow aquifers. An exception to this can be observed in the samples collected in February, as an unusual spike in concentration occurs. This sample was collected during an extreme rainfall event, where significant flooding had taken place. This indicates that significant levels of rainfall and rising groundwater levels in the shallow aquifers causes significant mixing with the deeper aquifers and other sources of contamination. Discussions with Affinity Water revealed that periods of heavy rainfall often cause spikes in concentrations as contamination can migrate more freely from distant sources. Therefore the source of this higher metaldehyde concentration may not be Smallford landfill alone. This spike in concentration was also observed in the River Colne, which typically showed relatively low background concentrations of metaldehyde, but rose above 1 µg L^{-1} during this time. Such an extreme spike is not observed in the data trend of the deeper chalk aquifers, again suggesting a degree of confinement from the shallow aquifers.

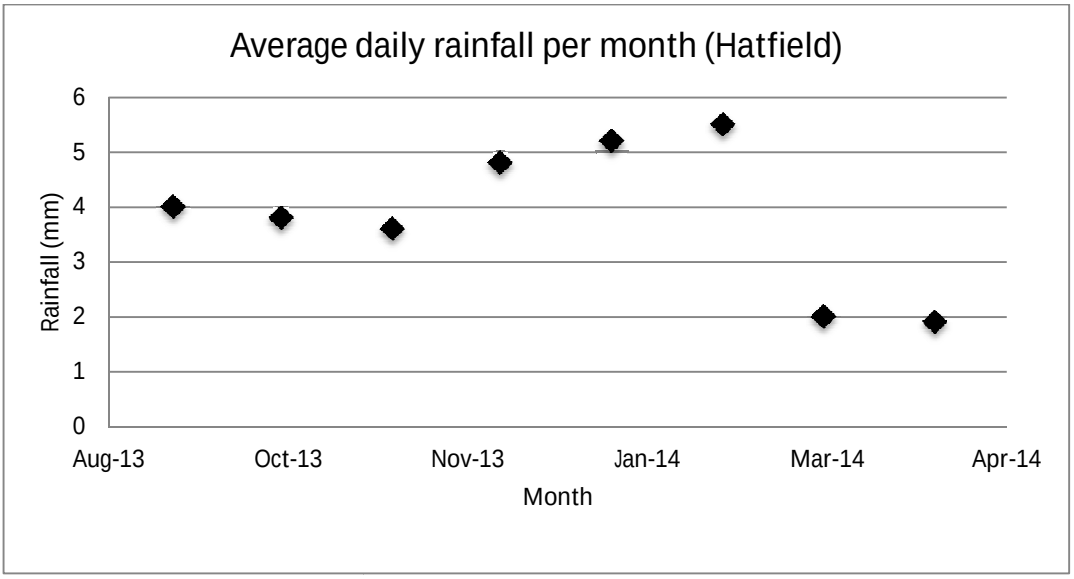


Figure 22: Average daily rainfall per month in Hatfield

Figure 22 shows a plot of the average rainfall per month for this area. Some similarities can be seen between the trends in metaldehyde concentrations of the chalk boreholes and the average daily rainfall per month. This relationship is less obvious when compared to shallow water sources such as CM3 and the River Colne. When the metaldehyde concentrations are plotted against rainfall, a subtle relationship between the two can be observed, as shown in Figure 23. The slight incline highlighted by the trendline shows that a higher rainfall could have an impact on the amount of contamination which enters the chalk aquifer. However, as this relationship is not particularly strong, it is likely that the contamination is affected by other factors such as groundwater levels and temperature.

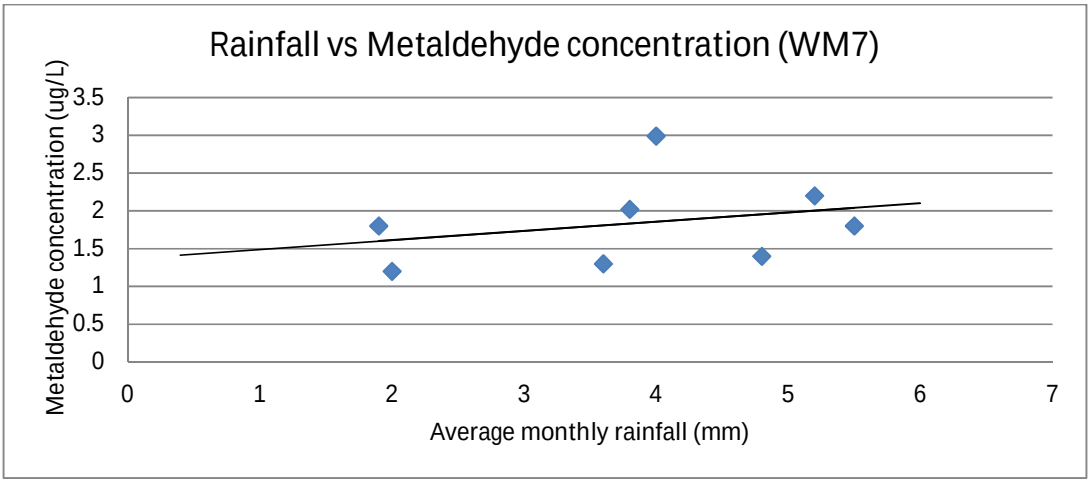


Figure 23: Demonstration of the subtle relationship observed between rainfall and metaldehyde concentrations at borehole WM7

The possible relationship between rainfall and metaldehyde concentration suggests that higher levels of percolating rainfall through the landfill results in a further direct contamination of the chalk aquifer. This could mean that the landfill cuts directly into the chalk in some areas. Significant cutting into the chalk aquifer is unlikely as this would cause the shallow aquifers to drain straight into lower chalk aquifer, and the constant abundance of water in the shallower boreholes indicates that this is not the case. However, the previously mentioned studies by Wu et al (2012) and Reddy et al (2011) suggest that the older and more compacted waste at the base of the landfill will have limited hydraulic conductivity, potentially limiting the flow of water into the chalk aquifer. As discussed regarding the Helpston site, metaldehyde could accumulate in this dense, water-retaining layer. Periods of heavy rainfall could then cause higher degrees of flushing of the deeper levels, releasing contamination into the chalk aquifer. This theory gives evidence to the presence of limited discrete pathways into the chalk, which are constant but not significant enough to drain the landfill cell and shallow aquifers entirely. It may also be the case that metaldehyde leaches more efficiently through the chalk and waste medium than water itself. Such cases of the diffusive transport of volatile compounds have been highlighted in a study by Tuncer, (2003).

Though the ability of metaldehyde to adsorb to solid mediums has not been well studied, it is possible that leached metaldehyde binds and accumulates within the solid medium (chalk). Periods of heavier rainfall could cause this accumulated metaldehyde to desorb from the solid rock and flow into the aquifer, giving an unexpected spike in concentration. This hypothesis would also account for the higher concentrations observed in the chalk aquifer. Similar to the observations at Helpston, the significantly higher concentrations which are seen at borehole WM7 could highlight a discrete source of metaldehyde located directly upstream of this borehole. This would explain the concentration difference observed with CM8A and would also account for the metaldehyde levels in the leachate wells being lower than that of WM7.

4.4 Other leachates

Leachate from a third landfill site located in the UK was also analysed and was found to contain metaldehyde. The compound was detected in two duplicate samples, however the results were not consistent. This is likely due to the strength of the leachate and the fine suspended solids preventing the extraction of a full 250 ml sample. The two duplicate samples were found to contain 6.1 and 12.4 μg L^{-1} metaldehyde. This was the first time metaldehyde had been found in this leachate, as it had not been previously looked for in analysis at the site. This evidence highlights that the link between metaldehyde and landfill could be more widespread than is currently known, and is likely to be often overlooked in the analysis of landfill leachate.

4.5 Conclusions

From the collected data, there is sufficient evidence to suggest that both landfill sites are a point source of metaldehyde. It is also clear that contaminant concentrations in the aquifer are governed by other variables such as rainfall (in the case of Smallford), and groundwater levels (as shown in the previous studies at Helpston). A lowering of its concentration with distance from the proposed point source was common to both of the sites due to the increasing

dilution of the contaminant as it migrates down the aquifer. The exceptions to this trend make it apparent that in each case there are preferential pathways for metaldehyde from the point-source. This can be caused by a discrete point-source of metaldehyde located in the landfill cells, or by a more complex path caused by adsorption to the solid aquifer mediums such as solid waste, chalk or sand. The studies by Wu et al (2012) and Reddy et al (2011) also show that preferential pathways are common in landfills as a result of the varying degrees of compaction and waste properties throughout a landfill cell. This was shown in each case by the significant differences in metaldehyde concentrations between neighbouring boreholes. The metaldehyde concentrations observed in the leachate wells at Smallford suggest that metaldehyde has a high degree of mobility through the landfill medium, and that metaldehyde concentrations show some degree of homogeneity throughout the landfill. Though the leachate wells do not show as high levels as WM7, perhaps not locating a discrete point-source, relatively consistent metaldehyde levels were still detected. If there is a discrete point-source, it is likely that any metaldehyde released from it rapidly spreads through the landfill. This high mobility is also supported by the large contamination spread observed at Helpston, with levels of 1.7 µg L^{-1} being observed some 3-5 km away from the point source. The detection of metaldehyde from a third landfill site also highlights that the metaldehyde problem at these sites could be common across many or all landfill sites. It is highly likely that the only recent development of the analytical method means that the compound is not routinely checked for in leachate analysis, and therefore may be overlooked in many cases.

5 Determination of the feasibility of an *in situ* synthesis of metaldehyde

5.1 Introduction

The emerging evidence from studies undertaken by water companies and the Environment Agency of England and Wales has shown a link between landfill sites and the contamination of the surrounding groundwater by metaldehyde. In many cases these detections were unexpected, as no record of metaldehyde disposal exists at the sites. This is most likely down to metaldehyde not being classed as a hazardous waste at the time the landfill sites were constructed and used. Pressure from the WFD and the DWI require that investigative actions be carried out to minimise the contamination of drinking and groundwater sources by pesticides and ensure they do not exceed the level of 0.1 μg L^{-1} in drinking water.

The unexpected detections of metaldehyde suggest that metaldehyde could potentially be synthesised *in situ* within a landfill site. It was hypothesised that landfill sites could provide suitable conditions, reagents and catalysts to induce the polymerisation of acetaldehyde, a simple, naturally occurring organic compound, to form metaldehyde. A literature review highlighted that the industrial process for metaldehyde synthesis involved the reaction of pure acetaldehyde with acidic and metallic catalysts at sub-zero temperatures, resulting roughly in an 8% yield of crystallised metaldehyde. Although these conditions cannot be met specifically in landfill, the potential for low aquifer temperatures, low leachate pH and the presence of acetaldehyde and metals in landfill suggested that some degree of *in situ* metaldehyde synthesis is feasible.

From this assessment of leachate chemistry, a viable mechanism was formulated accounting for the presence of water and acidic catalysts and the expected low yield of the metaldehyde product. It was confirmed from the literature that the metaldehyde synthesis was a reversible reaction and that metaldehyde yield was increased by optimising the reaction conditions. It could therefore be expected that any acetaldehyde within the landfill site could exist in

this equilibrium to form small amounts of metaldehyde. The verification of this hypothesis would allow more metaldehyde-specific remediation works to be carried out at landfill sites, and for the metaldehyde to be potentially declassified as a pesticide contaminant.

5.2 Methodology

A series of lab scale testing was designed based on the industrial conditions used to synthesise metaldehyde and the environmental conditions encountered in landfill and groundwater aquifers. The first series of tests were carried out to assess whether the reaction was feasible by simulating the industrial conditions in an aqueous solution containing high concentrations of acetaldehyde.

Subsequent tests were devised to determine whether pH variation or varying concentrations of calcium bromide catalyst had any effect on an aqueous solution of acetaldehyde. Using lower concentrations of reagents allowed a closer simulation of the real world conditions and therefore assess the likelihood of an *in situ* synthesis occurring in contaminated groundwater.

Test samples were prepared using VWR technical grade acetaldehyde and ultra-pure water. Acetaldehyde was diluted volumetrically to known concentrations and transferred into borosilicate glass bottles. Samples were then incubated under cold conditions (approximately 4 °C) to simulate the cold groundwater conditions and the colder temperatures used in the industrial synthesis. Where pH adjustment was required, concentrated hydrochloric acid or ammonia solutions were used where appropriate. After allowing for equilibration time, samples were analysed using the analytical method detailed in section 4.2.4 and analysed in triplicate.

In the first round of testing to determine the effects of pH, the procedure for involved diluting 10ml of pure acetaldehyde reagent in approximately 900ml of ultra-pure water. The pH was adjusted by the dropwise of addition of HCl or ammonia where appropriate. The adjusted solution was then diluted volumetrically to 1 litre and transferred to a borosilicate glass bottle. The second

round of pH testing used a single stock solution of dilute acetaldehyde. For each test, 200ml of the solution was taken and the pH was adjusted. The solution was diluted volumetrically to 250ml and transferred to 250ml borosilicate glass bottles and incubated in the same way. The use of this single stock solution allowed the removal of analytical errors involved with measuring small quantities of volatile acetaldehyde.

When assessing the effect of the calcium bromide catalyst on the acetaldehyde solution, the pH adjustment stage was replaced with the addition of solid calcium bromide.

The extent of acetaldehyde contamination was determined by dissolving 0.5 ml of pure acetaldehyde volumetrically in 1 litre of ultra pure water. The solution was then analysed in triplicate by taking three 250ml volumes of the solution.

5.3 Results and discussion

The initial results from the first pH tests are shown in Table 12. Whilst the results initially suggested than metaldehyde had been synthesised during incubation period (4 weeks), verification of the acetaldehyde solution used showed that significant levels of metaldehyde contamination were present in the pure acetaldehyde reagent. The extent of the contamination is discussed later in this section. The figures therefore demonstrate varying degrees of degradation of the metaldehyde contaminant in the acetaldehyde. Higher degradation is observed where more acidic conditions were used. It is also evident that metaldehyde degradation is less prevalent where the pH has been adjusted to milder and alkaline conditions, and that these conditions have more of a ‘preserving’ effect on the metaldehyde than a solution with no pH adjustment.

Aside from the unexpected metaldehyde contamination in the acetaldehyde reagent, the results were also contrary to the original hypothesis. The reaction mechanism adapted from the aldehyde polymerisation reaction by Greeves at al (2006) suggested that lower pH conditions would favour the synthesis of

metaldehyde, rather than aiding its degradation. The results therefore suggest that though the acidic conditions may have increased the rate at which acetaldehyde reacts with water to form its hydrate, the rate of polymerisation was not increased. It is likely that the acidic conditions promoted the oxidation process of the acetaldehyde to its carboxylic acid product, acetic acid. This process would have caused a decrease in pH, resulting in further oxidation of the remaining acetaldehyde reagent and the metaldehyde contaminant. It is also possible that the high abundance of water in the reaction mixture favoured the acetic acid product, rather than the polymerisation to metaldehyde.

The preservation of the metaldehyde contaminant at higher pHs can be explained by the ammonia molecules restricting the availability of protons in the solution. This would inhibit both the formation of the hydrate and the polymerisation mechanism. Any acetaldehyde successfully oxidised to its acetic acid form would immediately be neutralised by the basic ammonia, preventing further oxidation (degradation) of acetaldehyde and metaldehyde.

Table 12: Results demonstrating the effect of the pH on the test solutions

pH Value	Metaldehyde concentration after 4 weeks (μgL^{-1})	Average (μgL^{-1})
1.01 (Adjusted with HCl)	0.5	0.8
	0.5	
	1.5	
3.00 (Adjusted with HCl)	74.0	79.0
	85.0	
	78.0	
5.03 (Adjusted with NH_3)	199.5	194.2
	198.0	
	185.0	
7.00 (Adjusted with NH_3)	209.5	202.0
	192.0	
	205.0	

9.01 (Adjusted with NH_3)	201.5	196.5
	197.5	
	190.5	
4.01 (No adjustment)	187.5	175.0
	164.5	
	173.0	

This testing was repeated using a stock solution of diluted acetaldehyde, which was analysed immediately after diluting to determine its initial metaldehyde concentration. This acetaldehyde solution used in the reaction mixture was also analysed for metaldehyde to give an initial concentration for comparison. The results of this second round of testing and the calcium bromide tests are summarised in Table 13.

Table 13: Further testing demonstrating the effect of pH and a calcium bromide catalyst on the test solutions

Variable	Initial metaldehyde concentration of solution	Metaldehyde concentration after 1 week (μgL^{-1})	Average (μgL^{-1})
pH: 1.02 (Adjusted with HCl)	150.7	0.5	0.5
		0.5	
		0.5	
pH: 3.02 (Adjusted with HCl)	150.7	119.5	117.2
		115.5	
		116.5	
pH: 5.10 (Adjusted with NH_3)	150.7	153.0	151.0
		155.5	
		144.5	
pH: 7.16 (Adjusted with NH_3)	150.7	156.0	154.0
		153.0	
		153.0	
pH: 9.01 (Adjusted with NH_3)	150.7	158.0	150.3
		141.5	
		151.5	
$CaBr_2$ catalyst added: 0.1 g L^{-1}	154.7	154.0	145.3
		141.5	
		140.5	
$CaBr_2$ catalyst	154.7	145.0	144.5

added: 0.2 g L^{-1}		146.0	
		142.5	
$CaBr_2$ catalyst added: 0.5 g L^{-1}	154.7	153.5	146.3
		146.0	
		139.5	
$CaBr_2$ catalyst added: 1 g L^{-1}	154.7	145.5	130.8
		123.5	
		125.5	
$CaBr_2$ catalyst added: 2 g L^{-1}	154.7	111.5	134.3
		140.5	
		151.5	

As with the first pH testing round, lower pHs caused the metaldehyde to degrade significantly after only 7 days. It is also evident that milder pHs from 5 to 7 have little effect on the metaldehyde concentration. The addition of the calcium bromide catalyst had a negative effect on the initial concentration, with higher concentrations of bromide having further degrading effects. Although the use of a calcium bromide catalyst in the industrial synthesis of metaldehyde was confirmed in literature (Lonza Patents US3403168 and US1555223), its specific role in the reaction was not clear. It is therefore difficult to give precise reasoning for the metaldehyde degradation in these tests. However it is likely that the excess of water (which is not present in the industrial synthesis as pure acetaldehyde is used) had an effect. The dissolution reaction, which takes place between the water and calcium bromide, may have been more favourable than any reaction with the diluted aldehyde. The high solubility of calcium bromide in water gives evidence to this theory.

The contamination of the acetaldehyde reagent used throughout this testing was observed in a both bottle of acetaldehyde which had been opened for 2-3 weeks, and a freshly opened bottle of acetaldehyde from the same supplier. When contacted, the manufacturers of the acetaldehyde did not have any records of this contamination, and stated that the reversible polymerisation reaction, which takes place as acetaldehyde converts to metaldehyde is likely to vary depending on the storage conditions of the bottle. If correct, this would indicate that metaldehyde synthesis occurs within the bottle of pure

acetaldehyde reagent. It is also possible that the contamination was overlooked, as metaldehyde cannot be detected using conventional GC-MS scanning techniques, and must be specifically targeted in an analysis in order to be detected. Results of the analysis of acetaldehyde are shown in Table 14. It was found that the contamination of an opened bottle was higher than that of a freshly opened bottle. This may have been coincidence but may also suggest that some degree of *in situ* metaldehyde synthesis had occurred inside the bottle once it had been opened, as suggested by the supplier.

Table 14: Metaldehyde concentrations detected in two bottles of acetaldehyde of the same brand

Samples	**Metaldehyde concentration ($\mu g\ L^{-1}$)**	**Average ($\mu g\ L^{-1}$)**	**Metaldehyde concentration in pure acetaldehyde ($\mu g\ L^{-1}$)**
0.5ml of acetaldehyde from open bottle in 1l water	39.6	35.6	71200
	34.7		
	32.5		
0.5ml of acetaldehyde from freshly opened bottle in 1l water	22.5	22.4	44800
	22.5		
	22.1		

The unexpected contamination of acetaldehyde was investigated further to determine whether the batch of acetaldehyde tested was an isolated case, or whether the contamination could be a more widespread problem. Acetaldehyde of high purity from three alternative suppliers were tested in the same way. The results are summarised in Table 15.

Table 15: Extent of metaldehyde contamination from various suppliers of acetaldehyde

Manufacturer	Metaldehyde concentration ($\mu g\ L^{-1}$)	Metaldehyde concentration ($mg\ L^{-1}$)	Average ($mg\ L^{-1}$)
Merck	32000	32	28
	27000	27	
	24000	24	
Fisher	13000	13	13
	13000	13	
	13000	13	
Acros	10000	10	10
	10000	10	
	9000	9	

All bottles of acetaldehyde tested were found to contain metaldehyde contamination in the $mg\ L^{-1}$ level, even when described as an extra pure grade. This problem has not been previously reported in scientific literature and indicates a potential source of metaldehyde which could have been overlooked. Wastewater from industry containing traces of acetaldehyde could contain further traces of metaldehyde which could be overlooked in the quality analysis of the discharged water. Industrial waste containing acetaldehyde may also have been disposed of in landfill, causing a leaching of metaldehyde into the surrounding groundwater aquifer.

5.4 Conclusion

The testing has highlighted that *in situ* metaldehyde synthesis in landfill sites is highly unlikely. Simulating milder industrial conditions using an aqueous reaction medium and conditions that were more extreme than those observed in

landfill and groundwater aquifers failed to synthesise metaldehyde to a detectable level. Instead, it was observed that metaldehyde that was already present in the acetaldehyde solution degraded significantly at lower pHs which were hypothesised to be the closer to optimal synthesis conditions. It is therefore likely that low pH promoted the oxidation of the acetaldehyde to acetic acid, rather than the polymerisation mechanism to form metaldehyde. Degradation was also evident at higher pH values, though to a lesser extent. Calcium bromide, which is used as a catalyst in the industrial synthesis, was found to have no synthesising effect on the acetaldehyde, and did not have any preserving effect on the metaldehyde already present in the solution. This therefore suggests that the bromide catalyst had no noticeable effects on the reaction equilibrium between acetaldehyde and metaldehyde in an aqueous medium.

The demonstration of the infeasibility of an *in situ* synthesis reaction in water, combined with the evidence from the case studies shows that an *in situ* synthesis of metaldehyde at both of these sites is highly unlikely. It is more probable that metaldehyde from industrial and domestic sources was disposed of at these sites without being recorded as a hazardous waste. The fast degradation of metaldehyde in soils (Simms et al, 2006) may have been a reason as to why it was not regarded as a threat to groundwater. Its concentrations in groundwater would have also been overlooked for many years due to the only recent development of an analytical method. It is also likely that the action required by European legislation has caused this compound to emerge as a problem, when it had previously gone undetected. Evidence for how overlooked the issue could be is also provided by the unexpected metaldehyde concentrations in the leachate from a third landfill site and the indication of acetaldehyde as another source of the compound.

The project has also given some evidence about the mobility of metaldehyde within a landfill cell, with similar levels being detected in each of the leachate wells at Smallford. Evidence of its mobility was also shown at Helpston, which showed that metaldehyde can remain at detectable levels some 5km away from

the point-source. Evidence of preferential pathways taken by metaldehyde has also been highlighted, with different concentrations being observed in adjacent boreholes.

6 Areas for further research

Arguably, the most significant discoveries raised in this project were infeasibility of the *in situ* reaction, the unexpected detections of metaldehyde in the acetaldehyde reagents and the detection of metaldehyde in leachate from a third landfill site with no history of metaldehyde detection.

There is scope for the contamination of acetaldehyde to be further investigated via the analysis of different acetaldehyde sources. Investigation into the manufacturing process of acetaldehyde may also highlight how the contamination occurs and how it could be prevented. The exploring of this knowledge may also provide evidence that the *in situ* synthesis is possible within pure acetaldehyde. Other reagents linked with the industrial synthesis of metaldehyde such as paraldehyde could also be analysed to determine whether the contamination is even more widespread.

During this project, the feasibility of an experiment to synthesise acetaldehyde in the lab was assessed to see whether metaldehyde was a natural by-product of the synthesis process. However, the experiment could not be carried out due to time constraints and limited resources. Attempting the synthesis of acetaldehyde in a lab scale test in a variety of ways, such as the partial oxidation of ethanol, addition of water to acetylene and the direct oxidation of ethylene (the last of which is believed to be the most common process in industry) may show that metaldehyde is an overlooked by-product in some processes.

The collection of more data from other landfill sites with no history of metaldehyde contamination would also help to determine how widespread the metaldehyde problem is in landfill. The successful detection of metaldehyde in a one-off sample is unlikely to be by pure coincidence. Further study of the

concentrations at affected landfills will allow data sets to be compared and the chemical behaviour of metaldehyde in landfill to be further understood.

The studying of a variety of affected landfills though further groundwater sampling or a collaboration of various projects will also allow scope for the relationships of metaldehyde with various solid phases to be assessed. Both landfills studied in this project were limestone and chalk based, and therefore similar in their chemical composition (carbonate). The study of a metaldehyde contamination in a less porous medium such as a silicate rock would allow the diffusive and adsorptive properties of metaldehyde to be addressed and to help in predicting what affect different mediums will have on the leaching of metaldehyde from landfill.

Data providing evidence of acetaldehyde and paraldehyde concentrations in leachate and groundwater aquifers would also provide further to prove whether the acetaldehyde route of *in situ* synthesis was possible. If very low concentrations of acetaldehyde and paraldehyde were detected, it would show that this specific reaction equilibrium was non-existent within the landfill.

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